

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:)
Dennis J. Jones, Jr.) Art Unit: 1751
Application No.: 10/627,945) Examiner: Ogden Jr., N.
Filing Date: July 24, 2003) Confirmation: 3664
For: "METHODS OF TREATING AND)
CLEANING FIBERS, CARPET YARNS)
AND CARPETS")

APPEAL BRIEF

Mail Stop Appeal Brief - Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

NEEDLE & ROSENBERG, P.C.
Customer No. 23859

January 2, 2008

Sir:

The Appellant submits this brief in connection with the above-identified patent application (hereinafter "Application"). In view of this brief, the Appellant respectfully requests reversal of the rejections and allowance of the pending claims.

A Request for Extension of Time is enclosed herewith.

(1) REAL PARTY IN INTEREST

The real party in interest is Columbia Insurance Company, owner of the Application.

(2) RELATED APPEALS AND INTERFERENCES

There are no related appeals or interferences known to Appellant or the undersigned.

(3) STATUS OF CLAIMS ON APPEAL

Claims 45, 47-53, and 70-82 stand finally rejected by the Examiner in a final Office Action mailed May 17, 2007 ("Office Action"). The rejection of claims 45, 47-53, and 70-82 is being appealed.

(4) STATUS OF AMENDMENTS

No amendments have been filed subsequent to the Office Action.

(5) SUMMARY OF THE INVENTION

Independent claim 45 recites an aqueous treating composition [Page 5, line 30 – page 6, line 10] comprising tannic acid having a gallic acid content of less than about 1.0 parts by weight (pbw) [Page 6, line 12 – page 7, line 8; page 31, line 1 - 28], wherein the tannic acid is present in the aqueous treating composition at up to about 0.5 pbw, based on a total weight of the aqueous treating composition [Page 7, lines 1-7].

Independent claim 70 recites a two-part aqueous treatment [Page 19, lines 10-26; page 20, line 26 – page 21, line 22] comprising: a. a first aqueous treating composition comprising tannic acid [Page 6, line 12 – page 7, line 8; page 31, line 1 - 28]; and b. a separate second topical treating composition comprising a fluorochemical [Page 20, line 26 – page 21, line 22].

Independent claim 80 recites a fiber, yarn or carpet [Page 21, line 24 – page 24, line 6] comprising tannic acid [Page 21, lines 25-32] and a topically applied fluorochemical [Page 22, lines 4-12].

(6) GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

Whether claims 45, 47-50, and 52 are *prima facie* obvious over U.S. Patent No. 5,738,688 to De Lathauwer (hereinafter “De Lathauwer”). Whether claims 45, 47-50, and 52 are obvious over De Lathauwer.

Whether claims 45 and 47 are *prima facie* obvious over U.S. Patent No. 4,842,646 to Gamblin (hereinafter “Gamblin”). Whether claims 45 and 47 are obvious over Gamblin.

Whether claims 45 and 47 are *prima facie* obvious over U.S. Patent No. 4,094,701 to Fekete (hereinafter “Fekete”). Whether claims 45 and 47 are obvious over Fekete.

Whether claims 51 and 53 are *prima facie* obvious over De Lathauwer in view of U.S. Patent No. 5,520,962 to Jones, Jr. (hereinafter “Jones”). Whether claims 51 and 53 are obvious over De Lathauwer in view of Jones.

Whether claim 72 is *prima facie* obvious over De Lathauwer in view of Jones. Whether claims 70-76, and 78-82 are obvious over De Lathauwer in view of Jones.

Whether claim 77 is obvious over De Lathauwer in view of U.S. Patent No. 5,403,362 to Gurley (hereinafter “Gurley”).

(7) ARGUMENTS

The claims do not stand or fall together. Instead, the Appellant presents separate arguments for various independent and dependent claims. Each of these arguments is separately argued below and is presented with separate headings.

As there are no rejections under 35 U.S.C. §102 or 35 U.S.C. §112, the sole issue for appeal is the nonobviousness of the pending claims. Applicant asserts that the claims are nonobvious.

A. Rejection of claims 45, 47-50, and 52 under 35 U.S.C. §103(a).

Claims 45, 47-50, and 52 stand rejected as obvious over De Lathauwer. Claims 45 and 47 also stand rejected as obvious over Gamblin. Claims 45 and 47 also stand rejected as obvious over Fekete. Reversal of these rejections is respectfully requested for at least the reason that the Office Action has failed to set forth a legally sufficient *prima facie* obviousness rejection of the pending claims. Alternatively, reversal of these rejections is respectfully requested for at least the reason that Applicant's as-filed specification and responses during prosecution provided data evidencing unexpected and substantially superior results associated with the claimed compositions sufficient to overcome any *prima facie* obviousness rejection.

Each of claims 45, 47-50, and 52 recites a sub-range of gallic acid content (i.e., "a gallic acid content of less than about 1.0 parts by weight") within the recited tannic acid element. The Office Action contends that "[i]t would have been obvious to one of ordinary skill in the art, absent a showing to the contrary, to optimize the gallic acid content limitation of tannic acid because the prior art of record teaches and invites the inclusion of any commercial tannic acid." Office Action at ¶1, ¶2, ¶3, and ¶11 (citing *In re Peterson*, 315 F.3d 1325, 1330, 65 USPQ2d 1379, 1382 (Fed. Cir. 2003) (a copy is enclosed herewith in EVIDENCE APPENDIX)). The Action concedes that the cited references (i.e., De Lathauwer, Gamblin, and Fekete) fail to disclose or suggest a gallic acid content. *Id.* at ¶1, ¶2, and ¶3. Thus, the issue is whether a recited sub-range of gallic acid content within the tannic acid element is *prima facie* obvious over references that do not suggest the recited parameter.

The Patent Law recognizes two exceptions to the rule that it is obvious to discover an optimum sub-range by routine experimentation: (1) the sub-range optimized was not recognized to be a result-effective variable, and (2) the results of optimization were unexpectedly good for the sub-range. It is noteworthy that nonobviousness of unrecognized result-effective variables is acknowledged separately from nonobviousness of unexpectedly good results. That is, it is legally unnecessary to demonstrate both non-recognition of result-effectiveness and unexpectedly good results for a claimed sub-range to be nonobvious. However, while it is not

necessary to demonstrate unexpectedly good results for claimed sub-ranges wherein the result-effectiveness was unrecognized, Applicant has demonstrated both for these claims.

(1) Claims 45, 47-50, and 52 are not *prima facie* obvious over De Lathauwer, Gambin, and/or Fekete (individually or in combination) at least because the rejection is wrongly based upon the optimization of an unrecognized result-effective variable.

It is well-established that a “particular parameter must first be recognized as a result-effective variable, *i.e.*, a variable which achieves a recognized result, before the determination of the optimum or workable ranges of said variable might be characterized as routine experimentation.” MPEP § 2144.05(II)(B) (citing *In re Antonie*, 559 F.2d 618 (CCPA 1977) (emphasis added) (a copy is enclosed herewith in EVIDENCE APPENDIX)). Thus, the nonobvious optimization of unrecognized result-effective variables is an exception to the general rule:

In In re Aller . . . the court set out the rule that the discovery of an optimum value of a variable in a known process is normally obvious. We have found exceptions to this rule in cases where the results of optimizing a variable, which was known to be result effective, were unexpectedly good. . . . This case, in which the parameter optimized was not recognized to be a result-effective variable, is another exception.

In re Antonie, 559 F.2d 618, 620 (CCPA 1977) (emphasis added).

Thus, if a parameter is unrecognized to be result-effective, one of skill would not know to employ his or her routine skill to produce the claimed invention. Said another way, if a parameter is unrecognized to be result-effective, optimization of such a parameter would not even be obvious to try.

The opinions cited in the Office Action and by Applicant follow this rule. In *Peterson*, the claimed invention concerned “[a] nickel-base superalloy . . . consisting essentially of about 1 to 3 percent rhenium [and] about 14 percent chromium.” 315 F.3d at 1327. The Examiner had rejected the claim as obvious in view of the Shah reference, which disclosed “very broad ranges

for rhenium (0-7%) and chromium (3-18%).” *Id.* at 1328. The Court upheld the rejection and held that “selecting a narrow range from within a somewhat broader range disclosed in a prior art reference is no less obvious than identifying a range that simply overlaps a disclosed range.” *Id.* at 1330 (emphasis added). Therefore, when a prior art reference recognizes that parameters (*e.g.*, rhenium content and chromium content) are result effective, it can be *prima facie* obvious to optimize those parameters.

In contrast, *In re Antonie*, 559 F.2d 618, 195 USPQ 6 (CCPA 1977), the claimed invention concerned a wastewater treatment device with a ratio of tank volume to contactor area of 0.12 gal./sq. ft., the optimum value in that it maximizes “treatment capacity” so that the effectiveness of a given contactor is maximized. The Examiner had rejected the claim as obvious in view of the El-Naggar reference, which disclosed the basic device in question, but failed to teach a ratio of tank volume to contactor area. *Id.* at 619. The Court reversed the rejection, holding that “[i]t is impossible to recognize, from . . . El-Naggar, that ‘treatment capacity’ is a function of ‘tank volume’ or the tank volume-to-contactor area ratio. Recognition of this functionality is essential to the obviousness of conducting experiments to determine the value of the ‘tank volume’ ratio which will maximize treatment capacity.” *Id.* at 620 (emphasis added). Therefore, when the prior art fails to recognize a that parameter (*e.g.*, tank volume to contactor ratio) is result effective, it is nonobvious to optimize those parameters.

With respect to the pending claims, the Office Action failed to establish that any of the cited references – much less the skilled artisan – recognized that gallic acid content within tannic acid could achieve a recognized result. As such, while it may be arguably within the ordinary skill in the art to optimize a tannic acid concentration in view of the cited references, there is simply no disclosure in any of the cited references that evidences a recognition of any relationship whatsoever between gallic acid content and effectiveness of stain resistance. Moreover, the Office Action ignored its burden to set forth a legally sufficient *prima facie* rejection by making a bald assertion of obviousness and improperly shifting the burden upon the Applicant to show the sub-range of gallic acid content is unrecognized. Office Action at ¶1, ¶2, and ¶3 (“It would have been obvious . . . absent a showing to the contrary, to optimize . . .).

(2) Claims 45, 47-50, and 52 are not obvious over De Lathauwer, Gambin, and/or Fekete (individually or in combination) at least because Applicant provided data evidencing unexpected and substantially superior results associated with the claimed compositions sufficient to overcome any *prima facie* obviousness rejection.

It is well-established that, even if a *prima facie* case is established, “the presumption will be rebutted if it can be shown . . . that there are new and unexpected results relative to the prior art.” *Iron Grip Barbell Co. v. USA Sports, Inc.*, 392 F.3d 1317, 1322 (Fed. Cir. 2004) (a copy is enclosed herewith in EVIDENCE APPENDIX). While Applicant asserts that the pending claims are not *prima facie* obvious, Applicant’s Response of February 26, 2007, enclosed the declaration of Dennis J. Jones, Jr. under 37 C.F.R. § 1.132 (hereinafter “Jones Declaration”) (a copy is enclosed herewith in EVIDENCE APPENDIX), which demonstrated that compositions comprising tannic acid having the recited sub-range of gallic acid content provide fiber, yarn, or carpet having unexpected and substantially superior stain resistance.

When determining whether a *prima facie* case of obviousness has been overcome, the examiner must consider all rebuttal evidence. MPEP §2144.08B. In fact, once a nexus between the evidence and the claimed invention is established, the evidence is entitled to substantial weight. *Id.* While the submitted evidence should be commensurate in scope with claimed invention, an examiner cannot require the applicant to show unexpected results over the entire range of properties possessed by a composition. MPEP §2144.08B. Indeed, evidence showing that a claimed composition possesses superior and unexpected properties in one of a spectrum of common properties can be sufficient to rebut a *prima facie* case of obviousness. *Id.* In fact, a showing of unexpected results for a single member of a claimed subgenus is sufficient to rebut a *prima facie* case of obviousness if a skilled artisan “could ascertain a trend in the exemplified data that would allow him to reasonably extend the probative value thereof.” *Id.*

The Jones declaration established such a nexus by showing that objective evidence of nonobviousness (i.e., compositions having the recited sub-range of gallic acid content produce fibers significantly more resistant to “browning” – indicating superior stain resistance) are attributable to the claimed invention (i.e., compositions having less than 1% gallic acid have

superior stain resistance, while compositions having gallic acid contents outside the claimed range are less stain resistant). Moreover, the Jones Declaration established criticality of the claimed sub-range by comparing stain resistance when using tannic acids having gallic acid contents within the claimed range (e.g., 0.96%) to tannic acids having gallic acid contents outside the claimed range (e.g., 5.26% and 12.05%). *See* Jones Declaration at ¶¶16-24. Because the cited references (in particular, the De Lathauwer reference) completely fail to address gallic acid content, Applicant compared the superior results obtained from the claimed gallic acid content ranges to the gallic acid contents in a variety of commercially available tannic acids (e.g., “any commercial tannic acid can be used.”). Close inspection of the specification’s examples reveals that procedures analogous, if not identical, to those used in the De Lathauwer reference were employed. Direct comparison of the claimed subject matter (e.g., 0.96%) to the closest examples outside the claimed range reveals substantially superior results.

Because the all of the cited references completely failed to address gallic acid content, the substantially superior results due to the claimed gallic acid content that were demonstrated in the Jones declaration were unexpected to those of skill in the art at the time the invention was made. This conclusion is further supported by the Jones Declaration at ¶¶23-24.

B. Rejection of claims 51 and 53 under 35 U.S.C. §103(a).

Claims 51 and 53 stand rejected as obvious over De Lathauwer in view of Jones. Reversal of these rejections is respectfully requested for at least the reason that the Office Action has failed to set forth a legally sufficient *prima facie* obviousness rejection of the pending claims. Alternatively, reversal of these rejections is respectfully requested for at least the reason that Applicant’s as-filed specification and responses during prosecution provided data evidencing unexpected and substantially superior results associated with the claimed compositions sufficient to overcome any *prima facie* obviousness rejection.

As in claims 45, 47-50, each of claims 51 and 53 recites a sub-range of gallic acid content (i.e., “a gallic acid content of less than about 1.0 parts by weight”) within the recited tannic acid element. As set forth above, De Lathauwer is completely silent with respect to gallic acid

content. Likewise, Jones does not make any disclosure regarding gallic acid; instead, the Office Action cites this reference for its disclosure of fluorochemicals. As such, the disclosure of Jones cannot remedy this flawed rejection. Thus, no *prima facie* obviousness rejection can be made when the cited references fail to recognize the relationship between gallic acid content and stain resistance.

Moreover, as set forth above, the Jones declaration established that compositions having the recited sub-range of gallic acid content produce fibers significantly more resistant to “browning” – indicating superior stain resistance. Therefore, even if a *prima facie* case had been made, claims 51 and 53 are nonobvious in view of the substantially superior results demonstrated and set forth in the application and the Jones Declaration.

C. Rejection of claims 70-76, and 78-82 under 35 U.S.C. §103(a).

Claims 70-76, and 78-82 also stand rejected as obvious over De Lathauwer in view of Jones. Reversal of these rejections is respectfully requested for at least the reason that Applicant’s as-filed specification and responses during prosecution provided data evidencing unexpected and substantially superior results associated with the claimed compositions sufficient to overcome any *prima facie* obviousness rejection.

Each of claims 70-76 and 78-79 recites, *inter alia*, a first aqueous treating composition comprising tannic acid; and a separate second topical treating composition comprising a fluorochemical. Similarly, each of claims 70-76 and 78-79 recites, *inter alia*, a fiber, yarn or carpet comprising a tannic acid and a topically applied fluorochemical.

De Lathauwer is silent with respect to a composition comprising a fluorochemical. Jones is silent with respect to a composition comprising tannic acid. The Office Action asserts that it would have been obvious to combine the teachings of De Lathauwer and Jones to arrive at the pending claims, arguing essentially that it would be obvious because the two references are directed to the same objective.

Applicant respectfully disagrees that these claims are obvious. As demonstrated in the Jones Declaration (see ¶¶25-30), the recited two two-part aqueous treatment provides unexpected and substantially superior stain resistance when applied to a fiber, yarn, or carpet. More specifically, the claimed two-part treatment produced fibers significantly more resistant to “browning” as well as having improved stain resistance in general, as summarized in the Table (and represented graphically in Graphs I-IV). See Jones declaration at pp. 9-12. In each graph, when the inventive examples (*i.e.*, a separate, topically applied fluorochemical was used) were substantially superior to the comparative examples (*e.g.*, De Lathauwer), irrespective of which commercially available tannic acid was employed. That is, the inventive examples (“K” in Graphs I-II and “L” in Graphs III-IV) exhibit significantly lower “browning” (Graphs I-II) and total stain (Graphs III-IV) than the comparative examples (“A” in Graphs I-II and “E” in Graphs III-IV). Conditions and results for each example used were listed in the Table. Again, close inspection of the specification’s examples reveals that procedures analogous, if not identical, to those used in the De Lathauwer reference were employed.

Neither the combination of tannic acid and a separate, topical fluorochemical treatment nor improved stain resistance resulting therefrom is disclosed or suggested anywhere in the cited references. Thus, Applicant asserts that the substantially superior results of the claimed combination demonstrated in the Jones Declaration were unexpected to those of skill in the art at the time the invention was made. Thus, in view of these data, the combination of a first aqueous treating composition comprising tannic acid and a separate second topical treating composition comprising a fluorochemical is not obvious.

Moreover, it is noted that claim 72 recites, *inter alia*, the element of “wherein the tannic acid has a gallic acid content of less than about 1.0 part by weight, based on a total weight of the aqueous treating composition.” As with claims 45 and 47-53, this claim cannot be *prima facie* obvious for at least the reasons set forth above (*i.e.*, failure of the cited references to recognize a relationship between gallic acid content and stain resistance).

D. Rejection of claim 77 under 35 U.S.C. §103(a).

Claim 77 stands rejected as obvious over De Lathauwer in view of Gurley. While the Office Action has expressly rejected claim 77 as obvious over De Lathauwer in view of Gurley, Applicant presumes that it is the intent of the Office Action to reject claim 77 as obvious over De Lathauwer in view of Jones and further in view of Gurley. In either case, Applicant disagrees with the rejection.

Again, claim 77 recites, *inter alia*, a first aqueous treating composition comprising tannic acid; and a separate second topical treating composition comprising a fluorochemical. As set forth in detail above, De Lathauwer is silent with respect to a composition comprising a fluorochemical, and Jones is silent with respect to a composition comprising tannic acid. Moreover, Gurley merely discloses the use of stannous chloride and does not remedy the deficiencies in the alleged combination of De Lathauwer and Jones.

For reasons analogous to that set forth with respect to claims 70-76, and 78-82, *supra*, any alleged *prima facie* obviousness of claim 77 would be overcome by the showing of unexpected and substantially superior results provided in the Jones Declaration. In view of these data, the combination of a first aqueous treating composition comprising tannic acid, wherein the first composition further comprises a crosslinking agent comprising stannous chloride, and a separate second topical treating composition comprising a fluorochemical is not obvious and is, therefore, allowable.

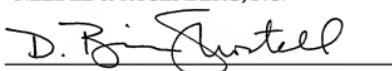
CONCLUSION

For at least the reasons set forth above, the Appellant respectfully requests reversal of the pending rejections.

A period was set for response, nominally ending the later of the balance of the two-month time period running from receipt of the notice of appeal mailed August 20, 2007, or one month from the mailing date of the Decision of Panel from Pre-Appeal Brief Review mailed October 2, 2007. Enclosed herewith is a Request for Two-Month Extension of Time, thereby extending the due date to January 2, 2008. Therefore, this paper is timely.

Payment in the amount of \$970.00, (reflecting the \$510.00 fee for Filing a Brief in Support of Appeal and the \$460.00 fee for the Request for Two-Month Extension of Time), is enclosed herewith. The payment is made electronically to be charged to a credit card. No further fee is believed due. However, the Commissioner is hereby authorized to charge any fees that may be required or credit any overpayment to Deposit Account No. 14-0629.

Respectfully submitted,
NEEDLE & ROSENBERG, P.C.


D. Brian Shortell, JD, PhD
Registration No. 56,020

NEEDLE & ROSENBERG, P.C.
Customer Number 23859
(678) 420-9300 Phone
(678) 420-9301 Fax

CERTIFICATE OF EFS-WEB TRANSMISSION UNDER 37 C.F.R. § 1.8

I hereby certify that this correspondence - including any items indicated as attached, enclosed, or included - is being transmitted by EFS-WEB on the date indicated below.


D. Brian Shortell, JD, PhD

January 2, 2008

Date

(8) CLAIMS APPENDIX

1-44. (canceled)

45. (previously presented) An aqueous treating composition comprising tannic acid having a gallic acid content of less than about 1.0 parts by weight (pbw), wherein the tannic acid is present in the aqueous treating composition at up to about 0.5 pbw, based on a total weight of the aqueous treating composition.

46. (canceled)

47. (previously presented) The treating composition of claim 45, wherein the tannic acid is present in the composition at from about 0.005 pbw to about 0.4 pbw.

48. (previously presented) The aqueous treating composition of claim 45 having a pH of less than about 3.0.

49. (previously presented) The aqueous treating composition of claim 45, further comprising:

- a) a stain resist compound;
- b) a crosslinking agent;
- c) a fluorochemical; or
- d) an organosilicate material.

50. (previously presented) The aqueous treating composition of claim 49, wherein the stain resist compound is present and comprises:

- a) a polymer or copolymer of methacrylic acid;
- b) a phenolic resin;
- c) styrene-maleic anhydride copolymer; or

- d) an aqueous emulsion of polymerized monomers, wherein the monomers comprise (meth)acrylic acid, alkyl (meth)acrylic acid, and a substituted or unsubstituted styrene.

51. (previously presented) The aqueous treating composition of claim 49, wherein the stain resist compound is present at from greater than 0.0 pbw to about 2.0 pbw solids, based on a total weight of the aqueous treating composition.

52. (previously presented) The aqueous treating composition of claim 49, wherein the crosslinking agent is present and comprises antimony potassium tartrate or stannous chloride.

53. (previously presented) The aqueous treating composition of claim 49, wherein the fluorochemical is present at from about 0.001 pbw to about 5.0 pbw, based on a total weight of the aqueous treatment composition.

54-69. (canceled)

70. (previously presented) A two-part aqueous treatment comprising:

- a. a first aqueous treating composition comprising tannic acid; and
- b. a separate second topical treating composition comprising a fluorochemical.

71. (previously presented) The aqueous treatment of claim 70, wherein the tannic acid has a gallic acid content of less than about 3.0 parts by weight, based on a total weight of the aqueous treating composition.

72. (previously presented) The aqueous treatment of claim 70, wherein the tannic acid has a gallic acid content of less than about 1.0 part by weight, based on a total weight of the aqueous treating composition.

73. (previously presented) The aqueous treatment of claim 70, wherein the first aqueous treating composition comprises an immersion bath.
74. (previously presented) The aqueous treatment of claim 70, wherein the second topical treating composition comprises a spray, a foam, or a combination thereof.
75. (previously presented) The aqueous treatment of claim 70, wherein the first aqueous treating composition further comprises a crosslinking agent.
76. (previously presented) The aqueous treatment of claim 75, wherein the crosslinking agent comprises antimony potassium tartrate.
77. (previously presented) The aqueous treatment of claim 75, wherein the crosslinking agent comprises stannous chloride.
78. (previously presented) The aqueous treatment of claim 70, wherein the second topical treating solution further comprises:
 - a. a stain resist compound;
 - b. a crosslinking agent; or
 - c. an organosilicate material.
79. (previously presented) The aqueous treatment of claim 78, wherein the stain resist compound is present in the second topical treating composition and comprises:
 - a. a polymer or copolymer of methacrylic acid;
 - b. a phenolic resin;
 - c. styrene-maleic anhydride copolymer; or
 - d. an aqueous emulsion of polymerized monomers, wherein the monomers comprise (meth)acrylic acid, alkyl (meth)acrylic acid, and a substituted or unsubstituted styrene.

80. (previously presented) A fiber, yarn or carpet comprising tannic acid and a topically applied fluorochemical.
81. (previously presented) The fiber, yarn or carpet of claim 80, wherein the tannic acid has a gallic acid content of less than about 3.0 parts by weight, based on a total weight of the aqueous treating composition.
82. (previously presented) The fiber, yarn or carpet of claim 80, wherein the tannic acid has a gallic acid content of less than about 1.0 part by weight, based on a total weight of the aqueous treating composition.

(9) EVIDENCE APPENDIX

Copies of cited case law are enclosed herewith:

In re Peterson, 315 F.3d 1325, 1330, 65 USPQ2d 1379, 1382 (Fed. Cir. 2003).

In re Antonie, 559 F.2d 618 (CCPA 1977).

Iron Grip Barbell Co. v. USA Sports, Inc., 392 F.3d 1317, 1322 (Fed. Cir. 2004).

A copy of the Declaration under 37 C.F.R. § 1.132 of Dennis J. Jones, Jr. is enclosed herewith (this declaration submitted by Applicant February 22, 2007, and addressed by examiner in Office Action).

Copies of references cited in Office Action are enclosed herewith:

U.S. Patent No. 5,738,688 to De Lathauwer.

U.S. Patent No. 4,842,646 to Gamblin.

U.S. Patent No. 4,094,701 to Fekete.

U.S. Patent No. 5,520,962 to Jones, Jr.

U.S. Patent No. 5,403,362 to Gurley.

(10) RELATED PROCEEDINGS APPENDIX

None.

315 F.3d 1325, *; 2003 U.S. App. LEXIS 233, **;
65 U.S.P.Q.2D (BNA) 1379

LEXSEE 315 F3D 1325

IN RE LANCE G. PETERSON and IOANNIS VASATIS

02-1129, (Serial no. 08/365,392)

UNITED STATES COURT OF APPEALS FOR THE FEDERAL CIRCUIT

315 F.3d 1325; 2003 U.S. App. LEXIS 233; 65 U.S.P.Q.2D (BNA) 1379

January 8, 2003, Decided

PRIOR HISTORY: [**1] Appealed from: United States Patent and Trademark Office Board of Patent Appeals and Interferences.

DISPOSITION: AFFIRMED.

LexisNexis(R) Headnotes

COUNSEL: James T. Hosmer, Nixon & Vanderhye P.C., of Arlington, Virginia, argued for appellants. With him on the brief was Leonard C. Mitchard.

William LaMarca, Associate Solicitor, Office of the Director of the United States Patent and Trademark Office, of Arlington, Virginia, argued for the Director. With him on the brief were John M. Whealan, Solicitor, and Joseph Piccolo, Associate Solicitor.

JUDGES: Before LOURIE, BRYSON, and DYK, Circuit Judges.

OPINIONBY: LOURIE

OPINION: [*1326] LOURIE, Circuit Judge.

Lance G. Peterson and Ioannis Vasatis (collectively, "Peterson") appeal from the decision of the U.S. Patent and Trademark Office ("PTO") Board of Patent Appeals and Interferences affirming the rejection of claims 1-7 of U.S. Patent Application 08/365,392 as obvious under 35 U.S.C. § 103. Ex Parte Wood, Appeal No. 1998-0535, Paper No. 19 (B.P.A.I. Apr. 23, [*1327] 2001). Because substantial evidence supports the Board's factual findings and the Board did not err in its conclusion of obviousness, we affirm.

BACKGROUND

On December 28, 1994, Mr. Peterson filed U. [*2] S. Patent Application 08/365,392, which is directed to a nickel-base single-crystal superalloy used in the manufacture of industrial gas turbine engines exposed to

high temperatures. The claimed composition includes a relatively small amount of rhenium and aims to improve a single-crystal alloy's mechanical strength without reducing its hot corrosion resistance. Representative claim 5 recites:

A nickel-base superalloy having special utility in the production of single crystal gas turbine engine blades consisting essentially of about 1 to 3 percent rhenium, about 14 percent chromium, about 9.5 percent cobalt, about 3.8 percent tungsten, about 2 percent tantalum, about 1.5 percent molybdenum, about 0.05 percent carbon, about 0.004 percent boron and, respectively, from about 3 to 4.8 percent aluminum, from about 4.8 percent to about 3 percent titanium, and balance substantially nickel.

(emphases added). Peterson and the Board considered that the other claims stand or fall with claim 5, and we will therefore consider only claim 5.

The examiner rejected claims 1-7 under 35 U.S.C. § 103 as obvious over the following prior art references: (1) [*3] published European Patent Application 240,451 ("Shah"); (2) published European Patent Application 076,360 ("Wukusick") alone or in view of U.K. Patent 2,153,848 ("Duhl"); and (3) U.S. Patent 3,619,182 ("Bieber") in view of Wukusick. For each ground of rejection, the examiner found a prima facie case of obviousness based on the overlapping element ranges of the prior art compositions and the claimed composition. Peterson responded by arguing that his invention would not have been obvious because the prior art disclosed only the optional use of rhenium and did not suggest that controlled amounts of rhenium would result in advantageous mechanical properties. Peterson also pointed to the unexpected results achieved by his

315 F.3d 1325, *; 2003 U.S. App. LEXIS 233, **;
65 U.S.P.Q.2D (BNA) 1379

invention: namely, the increased stress rupture life resulting from the addition of a small amount of rhenium. The examiner rejected those arguments in a final office action, finding that Peterson had failed to show criticality of the selected amount of rhenium commensurate in scope with the claims.

The Board affirmed the examiner's rejection. First, the Board found that the disclosure of overlapping ranges in Shah, Wukusick, and Bieber each established a prima facie case of obviousness. With respect to the rejection based primarily on Wukusick, the Board determined that the claimed range of "about 14 percent chromium" encompassed Wukusick's teaching to use up to 12% chromium. Secondly, the Board found that Peterson had failed to show that the claimed alloy possesses properties that would have been considered unexpected by a person of ordinary skill in the art. Specifically, the Board found that Peterson had not compared the claimed invention with the closest prior art (Wukusick's Alloy 2) and had not shown that the claimed range of rhenium was critical to improving stress rupture life. Thus, the Board concluded that Peterson's evidence of nonobviousness did not outweigh the evidence of obviousness and affirmed the examiner's rejection of claims 1-7.

Peterson timely appealed. We have jurisdiction pursuant to 28 U.S.C. § 1295(a)(4)(A).

[*1328] DISCUSSION

The ultimate determination whether an invention would have been obvious under 35 U.S.C. § 103 is a legal conclusion based on underlying findings of fact. *In re Kotzab*, 217 F.3d 1365, 1369, 55 USPQ2d 1313, 1316 (Fed. Cir. 2000). We [*1329] review the Board's legal conclusion of obviousness de novo and its underlying factual determinations for substantial evidence. *In re Gartside*, 203 F.3d 1305, 1316, 53 USPQ2d 1769, 1776 (Fed. Cir. 2000). Whether an invention has produced unexpected results and whether a reference teaches away from a claimed invention are questions of fact. *In re Mayne*, 104 F.3d 1339, 1343, 41 USPQ2d 1451, 1455 (Fed. Cir. 1997) (unexpected results); *Para-Ordnance Mfg. v. SGS Importers Int'l*, 73 F.3d 1085, 1088, 37 USPQ2d 1237, 1239 (Fed. Cir. 1995) (teaching away). Under the substantial evidence standard, we affirm the Board's factual determinations if they are based upon "such relevant evidence as a reasonable mind might accept as adequate to support a conclusion." *In re Gartside*, 203 F.3d at 1312, 53 USPQ at 1773 (quoting *Consolidated Edison Co. v. NLRB*, 305 U.S. 197, 217, 83 L. Ed. 126, 59 S. Ct. 206 (1938)).

On appeal, Peterson argues that the cited prior art does not establish a prima facie case of obviousness because it does not suggest the claimed combination of

"about 1 to 3 percent rhenium" with "about [**6] 14 percent chromium" to create an alloy having improved strength. As to the first ground of rejection, Peterson contends that a skilled artisan would not have assumed from Shah that using the claimed amounts of rhenium and chromium would improve alloy strength because Shah defines very broad ranges for rhenium (0-7%) and chromium (3-18%), mentions rhenium only as an optional ingredient, and discloses a preferred alloy containing no rhenium. With respect to the second ground of rejection, Peterson asserts that the Board misconstrued the phrase "about 14 percent chromium" to include 12% chromium. Peterson also argues that Wukusick only discloses the optional use of rhenium and does not suggest the combined use of rhenium and chromium in the amounts claimed. As to the final ground of rejection, Peterson argues that Bieber does not mention rhenium as a component in its alloys and even warns that increasing the chromium content to improve corrosion resistance will have "catastrophic effects" on other properties.

Peterson alternatively argues that, even if a prima facie case of obviousness were established, the Board erred in determining that the evidence of nonobviousness was insufficient [*1327] to rebut the prima facie case. Peterson points out that the claimed invention was the first to achieve the combination of corrosion resistance and improved strength for nickel-base single-crystal superalloys. Peterson thus contends that the examiner and the Board failed to appreciate the criticality of and the unexpected results achieved by the claimed combination of about 1-3% rhenium with, among other elements, about 14% chromium. Peterson further argues that Wukusick and Bieber teach away from the claimed invention by warning that high chromium contents can adversely affect alloy strength.

The PTO responds that the Board correctly found that the claimed composition would have been obvious based on any one of the three grounds of rejection because Shah, Wukusick, and Bieber all disclose ranges of elements that overlap the claimed ranges. The PTO argues that the Board properly interpreted the phrase "about 14 percent chromium" to include Wukusick's 12% chromium because Example 1 in Peterson's application discloses a superalloy containing 12.03% chromium.

[*1329] The PTO further responds that the Board correctly determined that Peterson failed to overcome the prima facie case of [*1328] obviousness. The PTO contends that substantial evidence supports the Board's findings that Wukusick does not teach away from the invention and that Peterson failed to show unexpected results. Specifically, the PTO points out that Peterson's specification shows improved performance in stress rupture life only for 2% rhenium, rather than for the full

315 F.3d 1325, *; 2003 U.S. App. LEXIS 233, **;
65 U.S.P.Q.2D (BNA) 1379

claimed range of about 1-3% rhenium, and that Peterson failed to compare his results with the closest prior art.

A. The Prima Facie Case of Obviousness

A prima facie case of obviousness typically exists when the ranges of a claimed composition overlap the ranges disclosed in the prior art. E.g., *In re Geisler*, 116 F.3d 1465, 1469, 43 USPQ2d 1362, 1365 (Fed. Cir.

1997); *In re Woodruff*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936-37 (CCPA 1976); *In re Malagari*, 499 F.2d 1297, 1303, 182 USPQ 549, 553 (CCPA 1974). Such is the case here. Claim 5 of Peterson's application recites and Shah discloses superalloys having the following compositions:

	Claim 5	Shah
Rhenium	about 1-3%	0-7%
Chromium	about 14%	3-18%
Cobalt	about 9.5%	0-20%
Tungsten	about 3.8%	0-18%
Tantalum	about 2%	0-15%
Molybdenum	about 1.5%	0-4%
Carbon	about 0.05%	at least 0.002%
Boron	about 0.004%	at least 0.002%
Aluminum	about 3-4.8%	3-8%
Titanium	about 4.8% to 3%	0-5%
Nickel	balance	balance

[**9]

Clearly, Peterson's application and Shah contain overlapping ranges, as each range listed in Peterson's claim 5 lies within the corresponding range disclosed in Shah. Thus, Shah's ranges encompass Peterson's.

Peterson argues that, despite that overlap, it would not have been prima facie obvious to select the claimed narrower ranges of rhenium and chromium from Shah's broader ranges of those elements. We disagree. In cases involving overlapping ranges, we and our predecessor court have consistently held that even a slight overlap in range establishes a prima facie case of obviousness. E.g., *In re Woodruff*, 919 F.2d at 1578, 16 USPQ2d at 1936-37 (concluding that a claimed invention was rendered obvious by a prior art reference whose disclosed range ("about 1-5%" carbon monoxide) abutted the claimed range ("more than 5% to about 25%" carbon monoxide)); *In re Malagari*, 499 F.2d at 1303, 182 USPQ at 553 (concluding that a claimed invention was rendered prima facie obvious by a prior art reference whose disclosed range (0.020-0.035% carbon) overlapped the claimed range (0.030-0.070% carbon)); see also *In re Geisler*, 116 F.3d at 1469, 43 USPQ2d at 1365 [**10] (acknowledging that a claimed invention was rendered prima facie obvious by a prior art reference whose disclosed range (50-100 Angstroms) overlapped the claimed range (100-600 Angstroms)). We have also held that a prima facie case of obviousness exists when the claimed range and the prior art range do not overlap but

are close enough such that one skilled in the art would have expected them to have the same properties. *Titanium Metals Corp. v. Banner*, 778 F.2d 775, 783, 227 USPQ 773, 779 (Fed. Cir. 1985) (concluding that a claim directed to an alloy containing "0.8% nickel, 0.3% molybdenum, up to 0.1% maximum iron, balance titanium" would have been prima facie obvious in view of a reference disclosing alloys containing 0.75% nickel, 0.25% molybdenum, balance titanium and 0.94% nickel, 0.31% molybdenum, balance titanium).

In light of that case law, we conclude that a prima facie case of obviousness was made out in this case. Selecting a narrow range from within a somewhat [*1330] broader range disclosed in a prior art reference is no less obvious than identifying a range that simply overlaps a disclosed range. In fact, when, as here, the claimed ranges [**11] are completely encompassed by the prior art, the conclusion is even more compelling than in cases of mere overlap. The normal desire of scientists or artisans to improve upon what is already generally known provides the motivation to determine where in a disclosed set of percentage ranges is the optimum combination of percentages. See *In re Boesch*, 617 F.2d 272, 276, 205 USPQ 215, 219 (CCPA 1980) ("Discovery of an optimum value of a result effective variable in a known process is ordinarily within the skill of the art." (citations omitted)). n1 We therefore conclude that a prior art reference that discloses a range encompassing a somewhat narrower claimed range is sufficient to establish a prima facie case of obviousness.

315 F.3d 1325, *; 2003 U.S. App. LEXIS 233, **;
65 U.S.P.Q.2D (BNA) 1379

That is not to say that the claimed composition having a narrower range is unpatentable. Rather, the existence of overlapping or encompassing ranges shifts the burden to the applicant to show that his invention would not have been obvious, as we discuss below. Accordingly, because Shah's ranges encompass Peterson's, we conclude that the Board did not err in determining that Shah renders Peterson's claimed composition *prima facie* obvious. n2 [**12]

n1 Although ranges that are not especially broad invite routine experimentation to discover optimum values, rather than require nonobvious invention, we do not have here any assertion that the disclosed range is so broad as to encompass a very large number of possible distinct compositions. We thus do not need to decide whether a disclosed range of such breadth might present a situation analogous to our cases involving the failure of a very broad disclosed genus of substances to render *prima facie* obvious specific substances within its scope. See, e.g., *In re Baird*, 16 F.3d 380, 29 USPQ2d 1550 (Fed. Cir. 1994); *In re Jones*, 958 F.2d 347, 21 USPQ2d 1941 (Fed. Cir. 1992).

n2 Consequently, we need not address the *prima facie* obviousness arguments based on the Wukusick, Duhl, and Bieber references. We note, however, that those references are less convincing than Shah in creating a *prima facie* case of obviousness. There is no genuine overlap between Wukusick's disclosed range of 7-12% chromium and Peterson's claimed range of "about 14 percent chromium." Peterson's only mention of an alloy having about 12% chromium is of a test alloy in its comparative Example I; it is not an example of Peterson's invention. Duhl and Bieber do not even mention rhenium, let alone disclose compositions with rhenium.

[**13]

B. Rebuttal of the Prima Facie Case

We turn next to Peterson's attempt to rebut the *prima facie* case of obviousness. In general, an applicant may overcome a *prima facie* case of obviousness by establishing "that the [claimed] range is critical, generally by showing that the claimed range achieves unexpected results relative to the prior art range." *In re Geisler*, 116 F.3d at 1469-70, 43 USPQ2d at 1365 (alteration in original) (quoting *In re Woodruff*, 919 F.2d at 1578, 16 USPQ2d at 1936). That same standard applies when, as here, the applicant seeks to optimize

certain variables by selecting narrow ranges from broader ranges disclosed in the prior art. See *In re Geisler*, 116 F.3d at 1470, 43 USPQ2d at 1365 ("Only if the 'results of optimizing a variable' are 'unexpected good' can a patent be obtained for the claimed critical range." (quoting *In re Antonie*, 559 F.2d 618, 620, 195 USPQ 6, 8 (CCPA 1977)); *In re Wertheim*, 541 F.2d 257, 267, 191 USPQ 90, 100 (CCPA 1976) (recognizing that "ranges which overlap or lie inside ranges disclosed by the prior art may be patentable if the applicant [**14] can show criticality in the claimed range by evidence of unexpected results"). Moreover, the applicant's showing of unexpected results must be commensurate in scope with the claimed range. See *In re Greenfield*, 571 F.2d 1185, 1189, 197 USPQ 227, 230 (CCPA 1978) [*1331] ("Establishing that one (or a small number of) species gives unexpected results is inadequate proof, for 'it is the view of this court that objective evidence of non-obviousness must be commensurate in scope with the claims which the evidence is offered to support.' (quoting *In re Tiffin*, 58 C.C.P.A. 1420, 448 F.2d 791, 792, 171 USPQ 294, 294 (CCPA 1971))).

We agree with the PTO that substantial evidence supports the Board's finding that Peterson failed to show that the addition of rhenium results in unexpected improvements in alloy strength for the entire claimed range of "about 1 to 3 percent" rhenium. The specification includes several examples of superalloy compositions and their respective strengths, measured by average rupture life. Of most relevance are the following data disclosed in those examples: Example I, which contains no rhenium, resulted in an average rupture life of about [**15] 34 hours. Example II, which includes 1% rhenium, resulted in an average rupture life of about 57 hours. Example III, which contains 2% rhenium, resulted in an average rupture life of about 114 hours.

Although those data show that alloy strength improved with the addition of rhenium, they do not evidence unexpected results for the entire claimed range of about 1-3% rhenium. From the few data points provided, the most significant improvement in stress rupture life occurred with the addition of 2% rhenium. However, the Board's implicit conclusion that the addition of rhenium in the lower portion of the claimed range did not produce unexpected results (i.e., the addition of 1% rhenium increased stress rupture life from 34 hours to only 57 hours) is supported by substantial evidence, and there are no data to show that the addition of rhenium in the uppermost portion of the claimed range (i.e., 3% rhenium) would lead to unexpected results. In fact, the only data that report the stress rupture life of an alloy having 3% rhenium seem to suggest the opposite. In an experiment similar to that demonstrated by Examples I-III, Example IV includes no rhenium and

315 F.3d 1325, *; 2003 U.S. App. LEXIS 233, **;
65 U.S.P.Q.2D (BNA) 1379

resulted in an average rupture [**16] life of about 148 hours. Example V, which contains 2% rhenium, resulted in an average rupture life of about 275 hours. Example VI, which contains 3% rhenium but less titanium than Examples IV and V, resulted in an average rupture life of only about 130 hours. Thus, the only data for an alloy containing 3% rhenium actually show a decrease in average rupture life as compared with alloys having 0% or 2% rhenium. Moreover, whether an applicant has shown unexpected results is a question of fact, on which we defer to the Board. We therefore conclude that substantial evidence supports the Board's finding that Peterson has not shown unexpected results that are commensurate in scope with the claimed range of "about 1-3 percent" rhenium.

Alternatively, an applicant may rebut a prima facie case of obviousness by showing that the prior art teaches away from the claimed invention in any material respect. *In re Geisler*, 116 F.3d at 1469, 43 USPQ2d at 1365 (quoting *In re Malagari*, 499 F.2d at 1303, 182 USPQ at 553). Peterson contends that the prior art teaches away from the claimed invention in that Wukusick teaches that the amount of chromium must be reduced [**17] when rhenium is added to a nickel-base superalloy for strength purposes. Peterson also argues that Bieber teaches away from the invention by warning that a high chromium content can have "catastrophic effects" on alloy strength. We agree with the PTO that substantial evidence supports the Board's finding that the prior art does not teach away from the claimed invention. Although the Board [*1332] did not expressly address "teaching away" in the context of Peterson's attempt to rebut the prima facie case of obviousness, it did find that the Shah, Wukusick, and Bieber references teach the invention and themselves establish prima facie cases of obviousness. Implicitly, then, the Board found that those references do not teach away from Peterson's invention. Certainly the Shah reference, the rejection on which we have affirmed the Board's decision, does not teach away from the invention. While it mentions a preferred alloy that does not contain rhenium, it does not disparage or otherwise discourage the use of alloys containing rhenium. Although Wukusick and Bieber may suggest upper limits on chromium content in order to avoid adverse effects on alloy strength, they disclose alloys containing [**18] as much as 12% and 14% chromium, respectively. Moreover, Wukusick expressly teaches that adding rhenium will improve high-temperature strength. Thus, substantial evidence supports the Board's factual finding that the prior art does not teach away from Peterson's combination of about 1-3% rhenium with about 14% chromium. We thus conclude that the Board did not err in its determination that Peterson failed to rebut the prima facie case of obviousness or in its ultimate

conclusion that Peterson's claimed superalloy would have been obvious under § 103.

CONCLUSION

Substantial evidence supports the Board's findings that Peterson's claimed element ranges are encompassed by the ranges disclosed in the Shah reference, that Peterson did not show unexpected results commensurate in scope with the claimed range of rhenium, and that the prior art does not teach away from the claimed invention. Thus, the Board did not err in concluding that claims 1-7 would have been obvious under § 103. Accordingly, the Board's decision is

AFFIRMED.

559 F.2d 618, *; 1977 CCPA LEXIS 118, **;
195 U.S.P.Q. (BNA) 6

IN THE MATTER OF THE APPLICATION OF RONALD L. ANTONIE

Patent Appeal No. 76-681.

UNITED STATES COURT OF CUSTOMS AND PATENT APPEALS

559 F.2d 618; 1977 CCPA LEXIS 118; 195 U.S.P.Q. (BNA) 6

AUGUST 18, 1977, Decided

PRIOR HISTORY: [**1]

Serial No. 331, 796.

COUNSEL:

Arthur H. Seidel, Thomas W. Ehrmann, Milwaukee, Wis. (Quarles & Brady, Milwaukee, Wis.), attorneys of record, for appellant.

Joseph F. Nakamura, Washington, D.C. for the Commissioner of Patents, R. D. Edmonds, Washington, D.C., of counsel.

OPINION BY:

BALDWIN

OPINION: [*618]

BALDWIN, Judge.

This is an appeal from a decision of the Patent and Trademark Office (PTO) Board of Appeals (board) affirming the rejection of claims 1, 2 and 3 of an application for "Rotating Biological Contactor Apparatus" n1/ as obvious under 35 USC 103 in view of El-Naggar, n2/ We reverse.

n1/ Serial No. 331, 796, filed February 12, 1973.

n2/ "Method of Treatment of Sewage by Bio-Oxidation and Apparatus Therefor," U.S. Patent No. 3,335,081, issued August 8, 1967.

The Invention

Appellant claims a wastewater treatment device in which wastewater is continuously passed through a tank. Semiimmersed contactors (disks) are continuously rotated to aerate their immersed portions and thereby to aeration both microorganisms that grow on the contactors and the wastewater itself. For this discussion, several

variables are important in this device. "Throughput" is the volume [**2] of wastewater per unit time (gal/day) which the device must treat. "Contactor area" is the total area of the contactors which is exposed to the wastewater as the contactors are rotated (sq. ft.). "Tank volume" is the actual volume of liquid in the tanks in which the contactors [*619] rotate (gal.). The ratio of throughput to contactor area (gal/day/sq. ft.) is called the "hydraulic loading." Two concepts of effectiveness of the equipment are important in this discussion. The primary prior art reference uses the term "efficiency" to denote the percent impurity reduction which a given set-up of the device achieves and we shall so use the term. Appellant uses the term "maximum treatment capacity" to denote when a unit of contactor area is providing maximum "efficiency" for a given "throughput" or maximum "throughput" for a given "efficiency." It is essential to understand the distinction between "efficiency," a matter of ultimate effectiveness independent of the efficiency of the equipment, and "treatment capacity," a matter of the efficiency or effectiveness of a unit of contactor area. The latter is more properly associated with the normal use of the term "efficiency" denoting [**3] maximum result from a limited resource.

Appellant's claimed device has a ratio of tank volume to contactor area of 0.12 gal./sq. ft. n3/ Appellant maintains that this ratio is the most desirable or optimum for all set-ups of the device in the sense that using a lower value gives lower "treatment capacity" and using a greater value gives no increase in "treatment capacity," merely increasing costs. Thus, the value is optimum in that it maximizes "treatment capacity" so that the effectiveness of a given contactor is maximized.

n3/ Claims 1 and 2 recite "at least about 0.12" while claim 3 recites "about 0.12."

The Prior Art

El-Naggar teaches the basic structure of the device claimed by appellant but is silent regarding quantitative

559 F.2d 618, *; 1977 CCPA LEXIS 118, **;
195 U.S.P.Q. (BNA) 6

design parameters other than to give data on a single example, which data was apparently complete except for any discussion of "tank volume." El-Naggar stated the "efficiency" (obviously referring to the purity of the output) could be increased to 95% by increasing the area of the contactor.

The Rejection

The examiner rejected the claims as obvious under 35 USC 103, noting that the basic device in question is old as taught by El-Naggar. [*4] While the ratio of tank volume to contactor area of 0.12 gal/sq. ft. is not disclosed in El-Naggar, the examiner reasoned that the disclosure of El-Naggar would make a device with that optimum value obvious. The examiner noted that El-Naggar suggests increasing the "efficiency" (degree of purification) of his device by increasing the contactor area while apparently keeping the "throughput" constant, that is, reducing the "hydraulic loading." The examiner then assumed that El-Naggar teaches keeping the tank volume constant while increasing the contactor area. Thus, the examiner argued that the idea of increasing tank volume to surface area to increase efficiency is taught and that working out the value for optimum efficiency is mere mechanical experimentation. The board accepted the examiner's reasoning.

OPINION

In determining whether the invention as a whole would have been obvious under 35 USC 103, we must first delineate the invention as a whole. In delineating the invention as a whole, we look not only to the subject matter which is literally recited in the claim in question (the ratio value) but also to those properties of the subject matter which are inherent in the subject [*5] matter and are disclosed in the specification. *In re Davies*, 475 F.2d 667, 177 USPQ 381 (CCPA 1973). In this case, the invention as a whole is the ratio value of 0.12 and its inherent and disclosed property. That property is that the described devices designed with the ratio will maximize treatment capacity regardless of the values of the other variables in the devices. Just as we look to a chemical and its properties when we examine the obviousness of a composition of matter claim, it is this invention as a whole, and not some part of it, which must be obvious under 35 USC 103. Cf. *In re Papesch*, 50 CCPA 1276, 315 F.2d 381, 137 USPQ 43 (1963). [*620]

The controlling question is simply whether the differences (namely the value of 0.12 and its property) between the prior art and appellant's invention as a whole are such that appellant's invention as a whole would have been obvious. The answer is no. It is impossible to recognize, from the experiment taught by El-Naggar, that "treatment capacity" is a function of "tank volume" or

the tank volume-to-contactor area ratio. Recognition of this functionality is essential to the obviousness of conducting experiments to determine [*6] the value of the "tank volume" ratio which will maximize treatment capacity. Such functionality can only be determined from data representing either efficiency at varying tank volume, fixed throughput, and fixed contactor area or throughput at varying tank volume, fixed efficiency, and fixed contactor area. Each of these experiments represents treatment capacity with fixed contactor area but varying tank volume. This sort of experiment would not be suggested by the teachings of El-Naggar since he was not trying to maximize or control "treatment capacity." The experiments suggested by El-Naggar do not reveal the property which applicant has discovered, and the PTO has provided us with no other basis for the obviousness of the necessary experiments.

The PTO and the minority appear to argue that it would always be obvious for one of ordinary skill in the art to try varying every parameter of a system in order to optimize the effectiveness of the system even if there is no evidence in the record that the prior art recognized that particular parameter affected the result. n4/ As we have said many times, obvious to try is not the standard of 35 USC 103. *In re Tomlinson*, 53 CCPA 1421, [*7] 363 F.2d 928, 150 USPQ 623 (1966). Disregard for the unobviousness of the results of "obvious to try" experiments disregards the "invention as a whole" concept of § 103, *In re Dien*, 54 CCPA 1027, 371 F.2d 886, 152 USPQ 550 (1967) and *In re Wiggins*, 55 CCPA 1356, 397 F.2d 356, 158 USPQ 199 (1968), and overemphasis on the routine nature of the data gathering required to arrive at appellant's discovery, after its existence became expected, overlooks the last sentence of § 103. *In re Saether*, 492 F.2d 849, 181 USPQ 36 (CCPA 1974).

n4/ The precise nature of the El-Naggar experiment and the nature of the data which would result are rendered hopelessly speculative by El-Naggar's total failure to discuss the critical matter of what is done with the volume of the tank. The PTO appears to assume, as a necessary element of its conclusion, that appellant's ratio is the inevitable result of El-Naggar's experiment, and that the tank volume is fixed, apparently because El-Naggar does not suggest changing the tank as additional contactor area is supplied. Even if the same tank were used, the actual liquid volume of the tank could change significantly if 1) the tank has a level control, 2) the tank is not extremely large in comparison to the contactors and 3) the volume-to-area ratio of the contactors themselves is significant. Since these

559 F.2d 618, *; 1977 CCPA LEXIS 118, **;
195 U.S.P.Q. (BNA) 6

assumptions are not unreasonable, there is serious doubt as to the constant volume of the tank.

Whether one would inevitably arrive at the ratio value of 0.12 or above depends on facts which must be read into El-Naggar, (e.g., the volume of the tank) and on assumptions about the kind of motivation (e.g., the degree of "efficiency" which would be sought). All of this involves, at least on this record, mere speculation. Assuming, as the examiner has, that the tank volume is fixed and the natural motivation is to maximize efficiency, if El-Naggar's equipment has a tank volume to contactor area ratio of less than 0.12, and the resulting efficiency is found wanting, increasing the contactor area to increase "efficiency" will lead away from the claimed ratio.

[**8]

In *In re Aller*, 42 CCPA 824, 220 F.2d 454, 105 USPQ 233 (1955), the court set out the rule that the discovery of an optimum value of a variable in a known process is normally obvious. We have found exceptions to this rule in cases where the results of optimizing a variable, which was known to be result effective, were unexpectedly good. In *re Waymouth*, 499 F.2d 1273, 182 USPQ 290 (CCPA 1974); In *re Saether, supra*. This case, in which the parameter optimized was not recognized to be a result-effective variable, is another exception. The decision of the board is reversed.

REVERSED

MILLER, J., concurs in the result.

DISSENT BY:

MALETZ

DISSENT: [*621]

MALETZ, Judge, */ dissenting, with whom RICH, Judge, joins.

a1/ Judge of the United States Customs Court sitting by designation pursuant to 28 USC 293(d).

With all due respect, I cannot agree with the majority's interpretation of the El-Naggar patent. El-Naggar discloses the same wastewater treatment apparatus as claimed, except for the specific volume-to-surface ratio of 12 gallons per square foot as recited in the claims. However, El-Naggar generally discloses varying the number of disks (column 3, lines 31-35), the number [*9] of concentric cylinders (column 4, lines 27-30), or the length of the cylinders (column 4, lines 61-

62) in his apparatus in order to optimize results. Given the basic apparatus of El-Naggar and the concept of varying the number of disks in a tank in order to optimize impurity removal, I believe that it would have been well within the capabilities of the chemical engineer of ordinary skill to determine empirically, by routine experimentation, the optimum design ratio which appellant has determined and recited in his claims. That is, El-Naggar set the way, and appellant's work was what any routineer would have accomplished in following the patent teachings.

Appellant urges that the results which he determined empirically by plotting the effect of volume-to-surface ratio on impurity removal, including the specific, optimum design ratio of 12 gallons per square foot, could not have been predicted from El-Naggar. However, obviousness under 35 USC 103 does not require absolute predictability, *In re Kronig*, 539 F.2d 1300, 190 USPQ 425 (CCPA 1976), and it is sufficient here that El-Naggar clearly led the way for the routineer to arrive at the claimed apparatus.

I am in substantial [**10] agreement with the board's analysis of this case, and I would affirm the board's decision.

**IRON GRIP BARBELL COMPANY, INC., Plaintiff-Appellant, and YORK
BARBELL COMPANY, INC., Plaintiff, v. USA SPORTS, INC., Defendant-
Appellee.**

04-1149

UNITED STATES COURT OF APPEALS FOR THE FEDERAL CIRCUIT

392 F.3d 1317; 2004 U.S. App. LEXIS 25769; 73 U.S.P.Q.2D (BNA) 1225

December 14, 2004, Decided

SUBSEQUENT HISTORY: Rehearing denied by, Rehearing, en banc, denied by *Iron Grip Barbell Co. v. USA Sports, Inc.*, 2005 U.S. App. LEXIS 3821 (Fed. Cir., Feb. 10, 2005)

PRIOR HISTORY: [*1]Appealed from: United States District Court for the Central District of California. Judge Gary L. Taylor.

DISPOSITION: Affirmed.

COUNSEL: Brian M. Daucher, Sheppard Mullin Richter & Hampton LLP, of Costa Mesa, California, argued for plaintiff-appellant. With him on the brief was Yael Karabelnik.

Terri G. Lewis, Wong, Cabello, Lutsch, Rutherford & Bruculeri, L.L.P., of Houston, Texas, argued for defendant-appellee. Of counsel was Louis Bruculeri.

JUDGES: Before NEWMAN, Circuit Judge, ARCHER, Senior Circuit Judge, and DYK, Circuit Judge.

OPINION BY: DYK

OPINION

[*1318] DYK, *Circuit Judge.*

Iron Grip Barbell Company ("Iron Grip") appeals from the judgment of the United States District Court for the Central District of California. The district court found claims 1 to 3 and 6 to 8 of Iron Grip's patent, U.S. Patent No. 6,436,015 ("the '015 patent"), to be invalid as obvious. We affirm.

[*1319] **BACKGROUND**

Iron Grip is a manufacturer of weight plates used with fitness equipment such as barbells and is the

assignee of the '015 patent. Claim 1 of the '015 patent claims:

A weight plate for physical fitness including: a plate body formed with a central throughbore and . . . further formed with solely a triad [*2] of spaced apart elongated handle openings disposed generally equiangularly . . . , said openings having respective outward edges cooperating with said plate to define a triad of integral handle elements for grasping by a single hand to effect transport of said weight plate.

Id. col. 4, ll. 24-35 (emphasis added). The other claims in the '015 patent at issue here depend from claim 1 and are not different for present purposes.

Typically, a barbell consists of a rigid bar and removable weight plates attached on both ends. Traditional weight plates had a single hole in the center for attachment to the barbell. A key problem with traditional single-hole weight plates was that they were difficult to grasp and transport. Iron Grip's '015 patent addresses this defect of traditional weight plates by disclosing a weight plate with three elongated openings near the periphery of the plate that function effectively as handles.

During the prosecution of the '015 patent, Iron Grip disclosed prior art showing, *inter alia*, weight plates with one elongated grip, U.S. Patent No. 4,199,140 ("the '140 patent"), and two elongated grips, U.S. Patent No. 5,137,502 ("the '502 patent"). [*3] The examiner further considered other prior art including barbell weight plates with four openings, U.S. Patent No. 4,618,142. After multiple rejections

on grounds of obviousness, the '015 patent eventually issued on Aug. 20, 2002.

USA Sports, Inc. ("USA Sports") is a competing manufacturer of weight plates. It also manufactures a three-grip plate. In May of 2002, Iron Grip sued USA Sports in the district court for infringement of an unrelated patent, and subsequently amended its complaint to state an action for infringement of claims 1-3 and 6-8 of the '015 patent. USA Sports defended on the basis that the asserted claims in the '015 patent were invalid as obvious in light of the prior art. Both sides moved for summary judgment. The district court initially granted summary judgment in favor of Iron Grip, finding that USA Sport's weight plate infringed the '015 patent; and denied USA Sport's summary judgment motion as to the invalidity of the '015 patent, holding that a finding of invalidity for obviousness required a "suggestion, motivation, or teaching in the prior art to combine the elements [from separate references]." (J.A. at 1897.) Upon motion for reconsideration, however, [**4] the district court held that the contested claims in the '015 patent were obvious. The district court found that its prior understanding of the law was "unduly restrictive." (J.A. at 2921.) Instead, it held that "the cases . . . permit the court to look at the overall picture of what's really going on The obviousness test . . . calls upon the court to just simply exercise common sense . . ." (*Id.*) Applying this new test, the district court held that "it would have been obvious to a layman to combine the prior art," and invalidated claims 1-3 and 6-8 of the '015 patent. (J.A. at 3.) Iron Grip appeals. We have jurisdiction pursuant to 28 U.S.C. § 1295(a)(1).¹

On appeal, USA Sports has not contested the finding of infringement except on the ground of invalidity.

[*1320] DISCUSSION

I

We review the district court's grant of summary judgment without deference. *Karsten Mfg. Corp. v. Cleveland Golf Co.*, 242 F.3d 1376, 1379 (Fed. Cir. 2001). We therefore affirm the [**5] district court only if there is no genuine issue of material fact as to the invalidity of the claims. In making this determination, a patent is presumed to be valid. 35 U.S.C. § 282 (2000); *Cardinal Chem. Co. v. Morton Int'l*, 508 U.S. 83, 93 n.15, 124 F.3d 2d 1, 113 S. Ct. 1967 (1993). USA Sports bears the burden of proving invalidity by clear and convincing evidence. *American Hoist & Derrick Co. v. Sowa & Sons, Inc.*, 725 F.2d 1350, 1360 (Fed. Cir. 1984).

In determining obviousness, we employ the four-part test set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 15 L. Ed. 2d 545, 86 S. Ct. 684 (1966). This test requires us to examine (1) the scope and content of the prior art; (2) the level of ordinary skill in the art; (3) the differences between the claimed invention and the prior art; and (4) the objective evidence of nonobviousness. *Id.* at 17-18; see also 35 U.S.C. § 103 (2000).

We note that neither side disputes that weight plates showing one, two and four elongated openings were within the prior art. We also note that neither side disputes that the proper level of ordinary skill in the art is [**6] that of a layman. Therefore, the only points of contention in the obviousness inquiry are the differences between the claimed invention and the prior art, and the objective evidence of nonobviousness.

II

We turn first to a comparison between the prior art and the claimed invention. In this inquiry, we are mindful of the repeated warnings of the Supreme Court and this court as to the danger of hindsight bias. See, e.g., *Graham*, 383 U.S. at 36 (consideration of secondary factors "serves to guard against slipping into use of hindsight and to resist the temptation to read into the prior art the teachings of the invention in issue" (internal quotations and citations omitted)); *In re Kotzab*, 217 F.3d 1365, 1369 (Fed. Cir. 2000) ("The very ease with which the invention can be understood may prompt one to fall victim to the insidious effect of a hindsight syndrome wherein that which only the invention taught is used against its teacher." (internal quotations omitted)). We note in this respect that the district court's use of an "overall picture" and "common sense" test of obviousness falls squarely into the hindsight trap. See *In re Lee*, 277 F.3d 1338, 1345 (Fed. Cir. 2002). [**7]

Where an invention is contended to be obvious based upon a combination of elements across different references, our cases require that there be a suggestion, motivation or teaching to those skilled in the art for such a combination. *In re Fine*, 837 F.2d 1071, 1074 (Fed. Cir. 1988). This requirement prevents the use of "the inventor's disclosure as a blueprint for piecing together the prior art to defeat patentability—the essence of hindsight." *Ecolochem, Inc. v. So. Cal. Edison Co.*, 227 F.3d 1361, 1371-72 (Fed. Cir. 2000) (quoting *In re Dembiczaik*, 175 F.3d 994, 999 (Fed. Cir. 1999)).

In this case, however, obviousness does not arise from any combination of elements from the prior art. Rather, the issue of the '015 patent's obviousness

arises because the prior art showed one, two and four elongated handles on weight plates. A single elongated handle on a weight plate was disclosed by the '140 patent. Two elongated handles on a weight plate was disclosed by the '502 patent. Four elongated handles on a [*1321] weight plate was disclosed by U.S. Design Patent No. 406,183 ("the '183 patent"). Reproductions of the two and four grip weight plates [*8] in the prior art, and Iron Grip's three-grip weight plate, appear below:

Fig. 1. The '502 patent's two-grip plate.

GET DRAWING SHEET 1 OF 1.

Fig. 2. The '183 patent's four-grip plate.

GET DRAWING SHEET 2 OF 2.

Fig. 3. The '015 patent's three-grip plates.

GET DRAWING SHEET 3 OF 3.

The key feature of the '015 patent, the fact that there are three elongated handles, falls within a range disclosed by the prior art. Where the "prior art . . . discloses a range encompassing a somewhat narrower claimed range," the narrower range may be obvious. *In re Peterson*, 315 F.3d 1325, 1330 (Fed. Cir. 2003). "When the difference between the claimed invention and the prior art is the range or value of a particular variable," then a patent should not issue if "the difference in range or value is minor." *Haynes Int'l v. Jessop Steel Co.*, 8 F.3d 1573, 1577 n.3 (Fed. Cir. 1993); see also *Titanium Metals Corp. of Am. v. Banner*, 778 F.2d 775, 783 (Fed. Cir. 1985) (invention found obvious because it was close to prior art range). Thus simply because [*9] an invention falls within a range disclosed by the prior art does not necessarily make it per se obvious. Both the genus and species may be patentable.

[*1322] Nonetheless, where there is a range disclosed in the prior art, and the claimed invention falls within that range, there is a presumption of obviousness. But the presumption will be rebutted if it can be shown: (1) That the prior art taught away from the claimed invention, *In re Geisler*, 116 F.3d 1465, 1471 (Fed. Cir. 1997); or (2) that there are new and unexpected results relative to the prior art, *In re Woodruff*, 919 F.2d 1575, 1578 (Fed. Cir. 1990).

There is, to be sure, one distinguishing feature of these range cases. Each involved a range disclosed within a single patent, while here the range is disclosed in multiple prior art patents. But, under the circumstances of this case, that is a distinction without a difference. The prior art suggested that a

larger number of elongated grips in exercise weights was beneficial,² thus plainly suggesting that one skilled in the art look to the range appearing in the prior art. The prior art disclosed weight plates with one, two and four elongated handles. [*10] Iron Grip is claiming a weight plate with three elongated handles, within the range of the prior art.

2 For example, U.S. Patent 4,673,179 describes a gymnastics weight with multiple handles as "very utilitarian" because it "enables a large number of grasping portions, and is very easily manipulated by the user." *Id.* col. 4, ll. 52-54.

It is also manifest that neither of the recognized exceptions applies here. First, Iron Grip offers no evidence that the prior art taught away from the invention besides the broad conclusory statement that "the prior art . . . taught towards fewer grips." (Reply Br. of Appellant at 14.) The prior art does not support this conclusion. There is no evidence of "sufficient teaching away." *In re Malagari*, 499 F.2d 1297, 1303 (C.C.P.A. 1974).

Second, there has been no showing that the three grips led to unexpected results.

Where "the difference between the claimed invention and the prior art is some range or other variable within the claims . . . , the [patenteel] [*11] must show that the particular range is critical, generally by showing that the claimed range achieves unexpected results." *Woodruff*, 919 F.2d at 1578. In the case of *In re Huang*, 100 F.3d 135 (Fed. Cir. 1996), we sustained a finding of obviousness in a situation somewhat similar to that involved here. In *Huang*, the claimed invention was a shock-absorbing grip with a polyurethane layer and a textile layer. The difference between the Huang grip and the prior art was that the Huang grip increased the thickness of the polyurethane layer relative to the textile layer, and had greater shock-absorbing qualities. There was nothing new or unexpected about this result because the prior art taught "that shock absorption derives in part from the compressible nature of the polyurethane layer. Given that the polyurethane layer absorbs shock, one of ordinary skill would logically infer that increasing the amount of the shock absorbing material (the polyurethane) would lead to an increase in the amount of shock absorption." *Id.* at 139. The invention was obvious because

Huang's contribution to the art could only lie in the specific thickness [*12] ratios recited in the claims. This court and its predecessors have

long held . . . that even though [a] modification results in great improvement and utility over the prior art, it may still not be patentable if the modification was within the capabilities of one skilled in the art, unless the claimed ranges "produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art."

[*1323] *Id.* (quoting *In re Aller*, 42 C.C.P.A. 824, 220 F.2d 454, 456, 1955 Dec. Comm'r Pat. 136 (C.C.P.A. 1955)).

There is no indication of any new and unexpected results from the use of a three-grip plate in the '015 patent or the prosecution history. The only benefit Iron Grip discloses in the patent regarding a three-grip plate is that "this construction allows a user to quickly find a handle element quickly [sic] and effortlessly." '015 patent, col. 4, ll. 3-4. There is no explanation why, as compared to the two or four grip plates in the prior art, a three-grip plate has advantages in this regard. A review of the prosecution history is likewise uninformative. In addition to the benefit of allowing a user to find a handle quickly and effortlessly, the [*13] examiner cites the ability of the user to grasp the handles of the plate with two hands at an appropriate angle as a reason for allowing the claim. (J.A. at 1237.) There is again no explanation of why such an effect could not likewise be achieved using a plate with two or four handles as existed in the prior art. We conclude that the patent and its prosecution history do not disclose any new and unexpected results from having three elongated grips on a weight plate. Nor has Iron Grip shown new and unexpected results based on evidence outside the patent and its prosecution history.

Finally, Iron Grip argues that *Huang* is inapposite because it was an appeal from the Board of Patent Appeals and Interferences ("Board"), and submits that it stands for the proposition of deference to the examiner and the Board. There is no merit to Iron Grip's contention. It is well-settled that "obviousness is a legal question based on underlying factual determinations," and in appeals from the Board "we review the ultimate legal determination of obviousness without deference." *In re Zurko*, 258 F.3d 1379, 1383-84 (Fed. Cir. 2001); see *In re McCarthy*, 763 F.2d 411, 412 (Fed. Cir. 1985). [*14] Here there is no factual issue. On the legal issue of obviousness (as opposed to the underlying factual issues) the grant of a patent does not create a

presumption of validity beyond the requirement that the party seeking to invalidate a patent must prove invalidity by clear and convincing evidence. *SSIH Equip. S.A. v. USITC*, 718 F.2d 365, 375 (Fed. Cir. 1983).

Because the claimed invention falls within a range disclosed in the prior art, and the patentee has not shown that the prior art taught away from the invention or new and unexpected results from a three elongated grip weight plate as compared to those in the prior art, we conclude that the claims are obvious absent substantial evidence of pertinent secondary factors supporting patentability.³

3 There is no claim here that expert testimony is required, the technology being simple. See *Centricut LLC v. Esab Group, Inc.*, 390 F.3d 1361, 2004 U.S. App. LEXIS 24977, Nos. 03-1574 & 03-1614, slip op. at 13-14 (Fed. Cir. Dec. 6, 2004). Indeed, both parties agree that the level of skill in the art is that of a layperson. (Br. of Appellant at 43; Br. of Appellee at 50.)

[**15] III

We now consider whether the patentee has demonstrated secondary evidence of nonobviousness. We have previously held that in "determining the question of obviousness, inquiry should always be made into whatever objective evidence of nonobviousness there may be." *Vandenberg v. Dairy Equip. Co.*, 740 F.2d 1560, 1567 (Fed. Cir. 1984); see also *Alza Corp. v. Mylan Labs*, 391 F.3d 1365, 2004 U.S. App. LEXIS 25446, No. 04-1344, slip op. at 12 n.9 (Fed. Cir. Dec. 10, 2004). The district court's opinion here did not consider the patentee's claimed evidence. "Our precedents . . . establish that failure to cite secondary [*1324] considerations, alone, is not reversible error." *Ruiz v. A.B. Chance Co.*, 234 F.3d 654, 668 (Fed. Cir. 2000). "Where the evidence of record is unchallenged as to secondary considerations ignored by the decision maker, this court may, as a matter of law, consider this objective evidence in reviewing the ultimate conclusion of obviousness/nonobviousness entered by the trial court" without the need for a remand. *Ashland Oil, Inc. v. Delta Resins & Refractories, Inc.*, 776 F.2d 281, 307 (Fed. Cir. 1985). Because in considering this record evidence, we conclude [*16] that it does not show the existence of relevant secondary factors to support patentability, we affirm the district court.

This court has previously identified, *inter alia*, commercial success, satisfaction of a long-felt need, and copying to be relevant factors in this inquiry. See *Demaco Corp. v. F. Von Langsdorff Licensing Ltd.*,

851 F.2d 1387, 1392 (Fed. Cir. 1988) (commercial success); *Uniroyal, Inc. v. Rudkin-Wiley Corp.*, 837 F.2d 1044, 1054 (Fed. Cir. 1988) (long-felt need); *Pro-Mold & Tool Co. v. Great Lakes Plastics, Inc.*, 75 F.3d 1568, 1574 (Fed. Cir. 1996) (copying).

Iron Grip has not made a showing of commercial success. Our cases make clear that a "nexus must be established between the merits of the claimed invention and evidence of commercial success before that evidence may become relevant to the issue of obviousness." *Solder Removal Co. v. USITC*, 65 C.C.P.A. 120, 582 F.2d 628, 637 (C.C.P.A. 1978). Ordinarily, this nexus may be inferred when "the patentee shows both that there is commercial success, and that the thing (product or method) that is commercially successful is the invention disclosed [**17] and claimed in the patent." *Demaco*, 851 F.2d at 1392.

The only evidence of marketplace success that Iron Grip proffers is that six retail competitors offered three-grip plates, and three of those competitors have entered into license agreements with respect to the '015 patent. (Br. of Appellant at 51.) Iron Grip does not explain the terms of the licenses nor the circumstances under which they were granted, except to concede that two were taken in settlement of litigation. (J.A. at 2121-22.) Our cases specifically require affirmative evidence of nexus where the evidence of commercial success presented is a license, because it is often "cheaper to take licenses than to defend infringement suits." *EWP Corp. v. Reliance Universal Inc.*, 755 F.2d 898, 908 (Fed. Cir. 1985). Thus we held in *In re GPAC Inc.*, 57 F.3d 1573 (Fed. Cir. 1995), that licenses "may constitute evidence of nonobviousness; however, only little weight can be attributed to such evidence if the patentee does not demonstrate a nexus between the merits of the invention and the licenses of record." *Id.* at 1580 (internal quotations and citations omitted). [**18] Without a showing of nexus, "the mere existence of . . . licenses is insufficient to overcome the conclusion of obviousness" when there is strong prima facie case of obviousness. *SIBIA Neurosciences, Inc. v. Cadus Pharm. Corp.*, 225 F.3d 1349, 1358 (Fed. Cir. 2000). There is no such evidence of a nexus here; hence the existence of licenses is of little significance.⁴

4 Whatever little significance the licenses may have is clearly outweighed by the strong evidence of obviousness found in the prior art. *Ruiz*, 234 F.3d at 668; *Brown & Williamson Tobacco Corp. v. Philip Morris Inc.*, 229 F.3d 1120, 1131 (Fed. Cir. 2000).

Iron Grip places significant emphasis on the fact that, before it filed for the '015 patent, there was no three-grip plate being offered in the retail market. It argues that the absence of such a three-grip [*1325] plate in light of the prior art speaks to the nonobviousness of its invention. However, Iron Grip has presented no evidence of a long-felt [**19] need for three-grip weight plates or the failure of others. Absent a showing of long-felt need or the failure of others, the mere passage of time without the claimed invention is not evidence of nonobviousness. See *In re Wright*, 569 F.2d 1124, 1127 (C.C.P.A. 1977).

Iron Grip also argues that USA Sports has copied its invention and this is objective evidence of nonobviousness. Our cases do establish that copying by a competitor may be a relevant consideration in the secondary factor analysis. *Vandenberg*, 740 F.2d at 1567. Not every competing product that arguably falls within the scope of a patent is evidence of copying. Otherwise every infringement suit would automatically confirm the nonobviousness of the patent. Rather, copying requires the replication of a specific product. This may be demonstrated either through internal documents, see *Akamai Techs., Inc. v. Cable & Wireless Internet Servs., Inc.*, 344 F.3d 1186, 1196-97 (Fed. Cir. 2003); direct evidence such as disassembling a patented prototype, photographing its features, and using the photograph as a blueprint to build a virtually identical replica, see *Advanced Display Sys., Inc. v. Kent State Univ.*, 212 F.3d 1272, 1285 (Fed. Cir. 2000); [**20] or access to, and substantial similarity to, the patented product (as opposed to the patent), *Cable Elec. Prods., Inc. v. Genmark, Inc.*, 770 F.2d 1015, 1027 (Fed. Cir. 1985), overruled on other grounds by, *Midwest Indus., Inc. v. Karavan Trailers, Inc.*, 175 F.3d 1356, 1359 (Fed. Cir. 1999) (en banc). The evidence of copying offered by Iron Grip is that USA Sports abandoned a one-grip plate and produced a three-grip plate after the '015 patent issued, despite receiving assurance from Iron Grip that a one-grip plate would not infringe Iron Grip's patent. (Br. of Appellant at 52-53.) This does not establish that USA Sports engaged in copying.

Since Iron Grip has not presented evidence of commercial success, satisfaction of a long-felt need, or copying, we conclude that there is no objective evidence to rebut the strong showing of obviousness based on the prior art.⁵

5 On appeal, Iron Grip does not argue that dependent claims 2-3 and 6-8 were improperly held to be obvious if the obviousness determination as to claim 1 is sustained. We interpret the district court's

judgment as reaching only the asserted claims (i.e. claims 1-3 and 6-8). Given our disposition it is unnecessary for us to consider the other alleged prior art submitted by USA Sports.

[**21] CONCLUSION

For these reasons, the district court's grant of summary judgment as to the invalidity of claims 3 1- and 8 6-of the '015 patent is

AFFIRMED.

COSTS

No costs.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Dennis J. Jones, Jr.

Application No.: 10/627,945

Filing Date: July 24, 2003

For: "METHODS OF TREATING AND
CLEANING FIBERS, CARPET YARNS AND
CARPETS") Art Unit: 1751
) Examiner: Ogden Jr., N.
) Confirmation: 3664
)
)
)DECLARATION UNDER 37 C.F.R. § 1.132 OF DENNIS J. JONES, JR.Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450NEEDLE & ROSENBERG, P.C.
Customer No. 23859
February 22, 2007

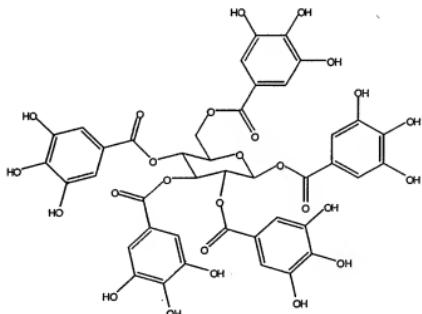
Sir:

The undersigned, Dennis J. Jones, Jr., a citizen of the United States, residing at 18 Ridge Rock Drive, Signal Mountain, Tennessee 37377, declares that:

1. I am the inventor listed on the above-identified application.
2. I hold a Bachelor of Science degree with a Biology major and Chemistry minor from the Berry College in Rome, Georgia and a Master of Science (undesignated) with studies in textile science from the Georgia Institute of Technology in Atlanta, Georgia.
3. I have been conducting research in the fields of textile science and engineering with emphasis on carpet manufacturing for twenty-five years, from 1981 to the present, and am listed as an inventor on at least three issued U.S. patents and at least five pending patent applications relating to carpet manufacture, carpet dyeing, and/or carpet protective treatment systems in general.

COPY

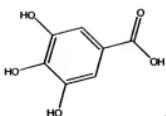
4. From June 1981 to the present, I have been employed in Dalton, Georgia as Director of Manufacturing Technical Resources for Shaw Industries, Inc., the largest carpet manufacturing company in the world.
5. As described in THE MERCK INDEX: AN ENCYCLOPEDIA OF CHEMICALS, DRUGS, AND BIOLOGICALS, THIRTEENTH EDITION 1615-16 (Maryadele J. O'Neil *et al.* eds., 2001) and HAWLEY'S CONDENSED CHEMICAL DICTIONARY 1067-68 (14th ed. 2001) (copies are attached hereto), tannic acids are well known in the art and comprise compounds derived from nutgalls having a structure of polygalloylglucose or polyalloylquinic acid. The sugar residue can be substituted with one or more residues of gallic acid, digallic acid, and/or trigallic acid. Tannic acid can have, for example, the following structure:



Note specifically the multiple ester functionalities that bind the gallic acid residues (carboxylic acid) to the sugar residue (alcohol) to form a tannic acid.

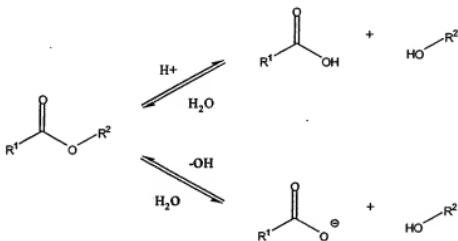
6. As described in THE MERCK INDEX: AN ENCYCLOPEDIA OF CHEMICALS, DRUGS, AND BIOLOGICALS, THIRTEENTH EDITION 772 (Maryadele J. O'Neil *et al.* eds., 2001) and HAWLEY'S CONDENSED CHEMICAL DICTIONARY 524 (14th ed. 2001) (copies are attached hereto), free gallic acid (3,4,5-trihydroxybenzoic acid) is one component of tannic acid that can be present in commercially-available tannic acids and has the following structure:

COPY



Note specifically that gallic acid is a carboxylic acid.

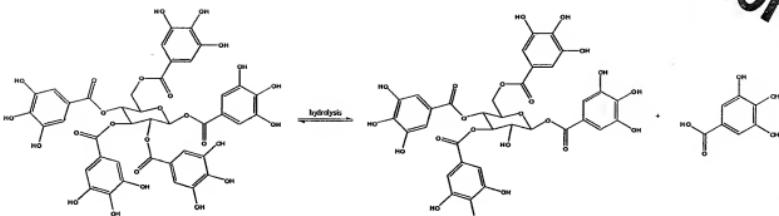
7. As described in J. March, ADVANCED ORGANIC CHEMISTRY: REACTIONS, MECHANISMS, AND STRUCTURE, THIRD EDITION 334-35 (1985) (a copy is attached hereto), ester hydrolysis is usually catalyzed by acids or bases and transforms a carboxylic acid into its constituent carboxylic acid (or salt thereof) and alcohol:



Thus, exposure of an ester to hydrolysis conditions results in a decrease in the starting materials (*i.e.*, ester and water) and an increase in the products (*i.e.*, alcohol and carboxylic acid or carboxylate salt).

8. As would have been readily understood by one of skill in the art, tannic acid comprises at least one carboxylic ester formed from 3,4,5-trihydroxybenzoic acid and a sugar (*e.g.*, glucose). Applying the reaction scheme referenced above to tannic acid, one of skill in the art would understand that tannic acid would have been hydrolyzed to produce 3,4,5-trihydroxybenzoic acid and a sugar derivative:

COPY



9. As a result, the free gallic acid (3,4,5-trihydroxybenzoic acid) content in tannic acid would have increased under hydrolysis conditions. The knowledge that hydrolysis would in fact increase the amount of free gallic acid within tannic acid actually teaches away from selecting tannic acids having less than about 1% gallic acid.
10. I have reviewed the Office Action mailed October 4, 2006, and the references cited therein. In particular, I have read and understood U.S. Patent No. 5,738,688 to De Lathauwer (hereinafter "De Lathauwer"), U.S. Patent No. 4,482,646 to Gamblin (hereinafter "Gamblin"), U.S. Patent No. 4,094,701 to Fekete (hereinafter "Fekete"), U.S. Patent No. 5,520,962 to Jones, Jr. (hereinafter "Jones"), and U.S. Patent No. 5,403,362 to Gurley (hereinafter "Gurley").
11. Based on my review of these references, it is my opinion that the claimed invention would have been unexpected and, therefore, would not have been obvious to one of ordinary skill in the art of carpet manufacture and carpet treatment at least because none of the cited references discloses a method of treatment that achieves the superior results of the claimed methods.
12. Based on my review of De Lathauwer, it is my opinion that the claimed invention would not have been obvious to one of ordinary skill in the art of carpet manufacture. While De Lathauwer states that any commercial tannic acid can be used, De Lathauwer does not suggest the selection of a tannic acid having a gallic acid content of less than about 1.0 part

COPY

by weight to practice its methods. In fact, De Lathauwer is silent as to the free gallic acid content of the tannic acid.

13. Further, based on my review of De Lathauwer, I conclude that one of ordinary skill in the art of carpet manufacture would not have been motivated by De Lathauwer to modify the gallic acid content to within the claimed amount. Because De Lathauwer provides no teaching as to the gallic acid content of the tannic acid, one having ordinary skill in the art of carpet manufacture would not have understood that stain resistance could have been improved by selecting a tannic acid having a certain gallic acid content, much less a gallic acid content of less than about 1.0 part by weight.
14. Based on the foregoing, I conclude that those of skill in the art would not have understood from De Lathauwer, or any other cited reference, that there was a relationship whatsoever between gallic acid content in tannic acid and improved stain resistance.
15. In contrast to the methods of De Lathauwer, the claimed invention relates to improved stain resistance observed when a treatment comprising tannic acid having less than 1 part by weight gallic acid is selected. Specifically, the compositions and methods of the present invention provide improved resistance to "browning," which can be caused by contact of fiber, yarn, or carpet with relatively high pH cleaning compositions, which are often used during routine maintenance of fiber, yarn, or carpet.
16. In order to demonstrate the superiority of the compositions and methods in the present application, the tests disclosed in the application were performed under my supervision. The tendency of fiber, yarn, or carpet to "brown" when contacted with high pH cleaning compositions was evaluated by measuring the color difference in a fiber, yarn, or carpet before and after application of a 10% by weight sodium hydroxide solution. The color difference was evaluated by using a Macbeth contact spectrophotometer model 20/20 ("Macbeth") and by using a visual gray scale rating system as described in ISO 105-A02 ("ISO 105-A02").

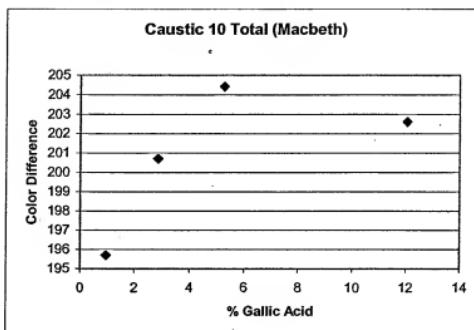
COPY

17. As described at page 31 of the specification, four tannic acids having differing gallic acid contents were evaluated. The "Caustic 10" test, using both the "Macbeth" and the "ISO 105-A02" measurement methods, was used to evaluate samples of treated fiber, yarn, or carpet, as set forth in Table 4 (page 38), Table 6 (page 41), Table 8 (page 44), and Table 10 (page 47) of the specification, as filed. Exemplary results are summarized below:

Tannic Acid	% Gallic	Caustic 10 (Macbeth)	Caustic 10 (ISO 105-A02)
ASP	0.96	195.7	17.5
3SP	2.87	200.7	16.5
CLM	5.26	204.4	16.5
BAYGARD® CL Liquid	12.05	202.6	16.5

18. As described at page 31 of the specification, tannic acids having differing gallic acid contents were evaluated in a "Caustic 10" test, using the "Macbeth" measurement method. A material treated with a tannic acid having 0.96% gallic acid provided a score of 195.7, while materials treated with a tannic acid having gallic acid contents of 2.87%, 5.26%, and 12.05% provided scores of 200.7, 204.4, and 202.6, respectively.

COPY

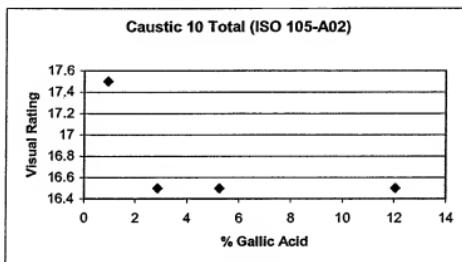


19. A lower "Macbeth" measurement for the Caustic 10 test denotes that the samples have a smaller change in coloration (*i.e.*, less "browning") due to exposure to a 10% by weight sodium hydroxide solution; this indicates superior stain resistance. Based upon these measurements as well as my visual comparison of a material treated with tannic acid having less than about 1% gallic acid with a material treated with tannic acid having greater than about 1% gallic acid, I conclude that there is a distinct improvement in stain resistance to "browning" for a material treated with tannic acid having less than about 1 part by weight gallic acid.

20. Likewise, as also described in the specification, tannic acids having differing gallic acid contents were evaluated in a "Caustic 10" test, using the "ISO 105-A02" measurement method. A higher "ISO 105-A02" measurement for the Caustic 10 test denotes that the samples appear less "browned" after exposure to a 10% by weight sodium hydroxide solution; this indicates superior stain resistance. A material treated with a tannic acid having 0.96% gallic acid provided a score of 17.5, while materials treated with a tannic acid having gallic acid contents of 2.87%, 5.26%, and 12.05% provided scores of 16.5, 16.5, and 16.5, respectively.

COPY

21. The visual rating ("ISO 105-A02") for samples contacted with a 10% by weight sodium hydroxide solution is unexpectedly higher for samples treated with tannic acid having less than about 1% gallic acid, as shown in the graph below:



22. Based on the resulting data, I conclude that the disclosed compositions and methods provide unexpectedly superior results when tannic acid having less than 1 part by weight gallic acid is selected as compared to compositions and methods of the prior art.

23. Based on all of the foregoing and on my knowledge of what those of skill in carpet manufacturing would have known, I conclude that those of skill in the art of carpet manufacture at the time the invention was made would not have reasonably expected that stain resistance to "browning" could have been improved by selecting and using a tannic acid having a gallic acid content of less than about 1.0 part by weight.

24. Thus, the substantially superior resistance to browning observed when using the claimed compositions to treat, e.g., fiber, yarn or carpet indicates that the claimed compositions are not obvious over De Lathauwer, Gamblin, Fekete, Jones, Gurley, or any combination thereof.

25. Additionally, unexpectedly superior stain resistance (for both total stain and for caustic) is achieved when applying a two-part aqueous treatment comprising a first aqueous treating composition comprising tannic acid and a separate second topical treating composition comprising a fluoroochemical.

COPY

26. The results from the Examples reveal that use of the claimed compositions provide a lower Caustic 10% (shown in Table as "Caustic") measurement (a lower number translates to decreased "browning") as well as a lower Total Stain (shown in Table as "Total") measurement (a lower number translates to improved resistance to staining in general). A summary of data from Tables 3-10 (see pages 37-47 of the specification as filed) is tabulated in the Table below:

Table

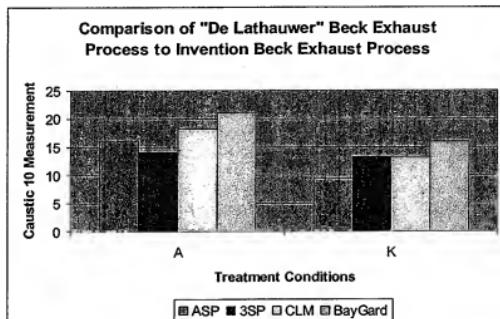
Sample Conditions		ASP (0.96%) ¹ Table 4, p.38		3SP (2.87%) ² Table 6, p.41		CLM (5.26%) ³ Table 8, p.44		BayGard CL (12.05%) ⁴ Table 10, p.47	
		Caustic	Total	Caustic	Total	Caustic	Total	Caustic	Total
A	Beck Exhaust (De Lathauwer)	16.2	104.9	14.2	76	18.3	104.8	21.1	80.5
B	Beck Exhaust (De Lathauwer) plus fluorochemical in bath	26.6	133.1	27.7	121.8	24.8	83.2	23	84.4
C	Beck Exhaust (conventional SR)	16.5	51.2	17	57.1	17.1	50.15	15.1	47.4
D	Beck Exhaust (conventional SR) plus fluorochemical in bath	15.7	56.3	14.8	47.4	16	56.3	13.4	47.4
E	Continuous (De Lathauwer)	16.4	108.4	15.5	107	20.9	94.5	22.4	104.8
F	Continuous (De Lathauwer) plus Alum	16.7	80.9	19.9	96.1	13.3	66.7	10.1	67.4
G	Continuous (De Lathauwer) plus fluorochemical in bath	16.2	90.1	16.4	87.5	16	71.3	21.9	84.9
H	Continuous (De Lathauwer) plus fluorochemical in bath plus Alum	15.3	78.5	14.4	82.4	11.7	67.8	11.5	67.1
I	Continuous (conventional SR)	18.9	93.2	13.1	82.4	15.5	89.9	17.5	99.1
J	Continuous (conventional SR) plus fluorochemical in bath	21.7	52.6	21.7	55.6	25.6	74.15	25.5	71.3
K	Invention (Beck Exhaust)	9.4	31.3	13.3	45.5	13.3	46.2	16	47.8
L	Invention (Continuous)	6.1	35.9	12.7	56.05	11.9	58.1	5.1	50.4

¹ Conditions for Samples A-L for ASP treated samples/controls are taken from Table 3, page 37.² Conditions for Samples A-L for 3SP treated samples/controls are taken from Table 5, page 40.³ Conditions for Samples A-L for CLM treated samples/controls are taken from Table 7, page 43.⁴ Conditions for Samples A-L for BayGard CL treated samples/controls are taken from Table 9, page 46.

COPY

27. For example, comparison of a Beck Exhaust process with treatment conditions analogous to those used in De Lathauwer (Table, entry A and Graph I, columns A) with a Beck Exhaust process with treatment conditions as claimed in the present invention (Table, entry K and Graph I, columns K) demonstrates that the claimed compositions, when compared to conventional compositions (e.g., De Lathauwer) provides a substantially superior caustic 10 measurement (here, as much as about, e.g., 42% lower).

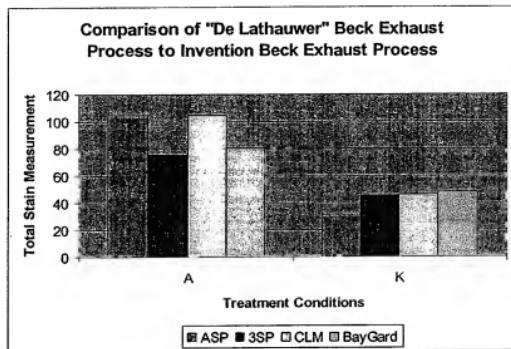
Graph I



28. Likewise, comparison of a Beck Exhaust process with treatment conditions analogous to those used in De Lathauwer (Table, entry A and Graph II, columns A) with a Beck Exhaust process with treatment conditions as claimed in the present invention (Table, entry K and Graph II, columns K) demonstrates that the claimed compositions, when compared to conventional compositions (e.g., De Lathauwer) provides a substantially superior total stain measurement (here, as much as about, e.g., 70% lower).

COPY

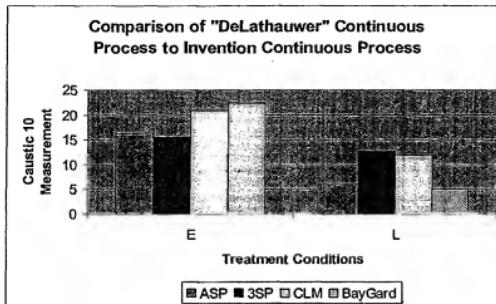
Graph II



29. Such improvement is also evident for the claimed methods in a continuous process. Comparison of a continuous process with treatment conditions analogous to those used in De Lathauwer (Table, entry E and Graph III, columns E) with a continuous process with treatment conditions as claimed in the present invention (Table, entry L and Graph III, columns L) demonstrates that the claimed method, when compared to conventional methods (e.g., methods analogous to De Lathauwer) provides a substantially superior caustic 10 measurement (here, as much as about, e.g., 63% lower).

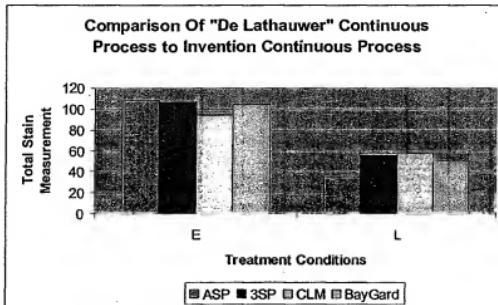
COPY

Graph III



30. Again, this improvement is also evident for the claimed compositions for total stain measurement in a continuous process. Comparison of a continuous process with treatment conditions analogous to those used in De Lathauwer (Table, entry E and Graph IV, columns E) with a continuous process with treatment conditions as claimed in the present invention (Table, entry L and Graph IV, columns L) demonstrates that the claimed compositions, when compared to conventional compositions (e.g., De Lathauwer) provides a substantially superior total stain measurement (here, as much as about, e.g., 67% lower).

Graph IV



COPY

31. No such improved stain resistance is disclosed or suggested anywhere in the cited references.

32. I declare that all statements made herein of my own knowledge and belief are true and that all statements made on information and belief are believed to be true, and further, that the statements are made with the knowledge that willful false statements are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dennis J. Jones, Jr.

Dennis J. Jones, Jr.

Dated: 2/21/97

US005738688A

United States Patent [19]

De Lathauwer

[11] Patent Number: 5,738,688

[45] Date of Patent: Apr. 14, 1998

[54] PROCESS TO IMPROVE RESISTANCE TO
STAINS ON FIBRES AND DERIVED
PRODUCTS

3,961,881 6/1976 Sumner et al.
4,501,592 2/1985 Ucci et al.
4,833,009 5/1989 Marshall.

[75] Inventor: Armand De Lathauwer, Aalst,
Belgium

FOREIGN PATENT DOCUMENTS

864576	4/1941	France .
53 081 788	12/1976	Japan .
61-174485	8/1986	Japan .
2-197579	8/1990	Japan .

[73] Assignee: N. V. Denderland-Martin, Gijzegem,
Belgium

OTHER PUBLICATIONS

[21] Appl. No.: 687,403

Chem. Abstracts, vol. 90, No. 4, 22 Jan. 1979, Abstract No.
24736d, Wada, Hideki, Prevention of staining of dyed silk
yarns.

[22] PCT Filed: Jan. 25, 1995

Database WPI, Section Ch, Week 8638, Derwent Publications
Ltd., London, GB; Class A11, AN 86-247834, Aug.
1986.

[86] PCT No.: PCT/BE95/00006

§ 371 Date: Aug. 2, 1996

§ 102(e) Date: Aug. 2, 1996

[87] PCT Pub. No.: WO95/21955

PCT Pub. Date: Aug. 17, 1995

[30] Foreign Application Priority Data

Feb. 2, 1994 [BE] Belgium 09400124

Primary Examiner—Alan Diamond
Attorney, Agent, or Firm—Pollock, Vande Sande & Priddy

[51] Int. Cl.⁶ D06M 13/238; D06M 15/41

[57] ABSTRACT

[52] U.S. Cl. 8/115.56; 8/116.1; 8/116.4;
8/120; 8/127.6; 8/115.56; 8/115.54; 8/137;
8/552; 8/594; 8/595; 427/389; 427/389.9;
427/393.4; 442/93; 428/365

The invention consists of a process to improve the resistance
to stains on fibres, processed or not, finished or not on the
basis of dyeable natural or synthetic fibres, in particular
polyamide. According to the invention the fibres are treated
with a solution containing tannic acid and a condensation
product of a sulphonated phenol- or naphol-derivative with an
aldehyde. The treatment can be made before, during or after
the dyeing process. The treatment is done in an acid
medium.

[53] Field of Search 8/116.1, 116.4,
8/120, 127.6, 115.56, 115.54, 137, 552,
594, 595; 427/389, 389.9, 393.4; 428/267,
278, 224, 365; 442/93

[56] References Cited

22 Claims, No Drawings

U.S. PATENT DOCUMENTS

2,342,823 2/1944 Schlack .

PROCESS TO IMPROVE RESISTANCE TO
STAINS ON FIBRES AND DERIVED
PRODUCTS

This application is a 371 of PCT/BIE95/00006 filed Jan. 25, 1995.

This invention relates to a process to improve the resistance to stains on dyable natural and synthetic fibres and in particular polyamide fibres.

By "fibres" has to be understood, fibres or yarns whether greige (raw) or processed, unfinished or finished, bright as well as dull, thermofixed or not, in yarn form or processed to fabric, felt, knitwear, non-wovens, carpets, rugs, etc. To simplify matters, in this description fibres in which form whatsoever will be called "substrate".

Removal of stains, coloured or not, from a substrate, is still a very delicate problem, as there could remain traces or spots either by discoloration or coloration of the original substrate caused by the stain or by the detergents which affect the dyestuff of the substrate. This is especially the case for stains caused by products containing chlorine, oxidative bleaching agents, and stains containing persistent dyestuffs or pigments for instance present in coffee, tea, wine, fruit juices, inks . . .

The purpose of this invention is to propose a process by which the resistance of a coloured or uncoloured substrate against stains of any nature is considerably improved whilst at the same time also other improved characteristics are obtained such as an improved antistatic behaviour, resistance to products such as turpentine and white spirit as well as resistance to soiling, mildew and house-mite.

It is known (C.A. Vol. 97 (1982) 7,704 U) that tannin is used to fix dyestuff after the dyeing process. On the other hand it is also known from the swimwear industry, to treat coloured nylon fabric with extraction's of gallotannin to improve the colour fastness to chlorine. This was based on the fact that the additional treatment of coloured nylon fabric with gallotannin extraction's caused a migration of the dyes in the fibre whereby the gallotannin is fixed on the fibre. This provides a certain resistance to discoloration of the substrate by products containing chlorine. However this treatment has no known effect on coloured stains, and on stains caused by other oxidative bleaching agents.

On the other hand, it is known from the U.S. Pat. No. 4,501,591, to treat polyamide fibres after application of the dyestuff, with condensation products of sulfonated phenol- or naphthal-formaldehydes in presence of an alkalinemetasilicate. It has been shown that for polyamide fibres, this treatment provides resistance to colour stains and particularly effective for anionic dyes. This treatment has no effect whatsoever on chlorine stains and on stains of other oxidative bleaching agents.

In the cosmetic industry, there is an increasing use of strong oxidative bleaching agents, such as benzoylperoxide. Resistance to stains caused by this type of products is unknown in the textile industry.

During extensive research in this field, it has now surprisingly been demonstrated that the resistance of coloured or uncoloured substrate to stains or to deterioration of the fibres caused by oxidative bleaching agents, is considerably improved when the substrate is treated with a solution containing tannic acid and a condensation product of a sulfonated phenol- or naphthal-derivative with an aldehyde.

It has also been found that this treatment is also very effective against stains caused by dyes of natural or synthetic origin of anionic, cationic, metalcomplex or disperse nature.

That the tannic acid would improve the discoloration caused by chlorine, could be expected by the man skilled in

the art, but that treatment with the solution mentioned above would be more efficient than a normal tannic acid treatment, could not be predicted.

Furthermore, the resistance to coloured stains obtained by a treatment with a condensation product of a sulfonated phenol- or naphthal-formaldehyde is not only met by the treatment with the solution according to the invention, but is considerably improved.

The effectiveness of the solution containing both components (tannic acid and condensation product) is not only better than that of the separate components, but also provides a protection against a wide range of coloured stains for which the individual components were not effective.

The interaction of these two components increases the efficiency of the individual components and provides unexpected additional properties, such as protection against coloured stains of cationic, metalcomplex and disperse nature, and especially against stains caused by oxidative bleaching agents.

According to the invention, the substrate, in acid medium is treated with a solution containing 1 to 6% (weight %) active component, consisting of 10 to 90%, preferably 40 to 80% tannic acid (tannic acid component) and 10 to 90%, preferably 20 to 60% condensation product of a sulfonated phenol- or naphthal-derivative with an aldehyde (sulphon component).

These concentrations and proportions are not critical, though it has been noticed that higher concentrations hardly influence the result but could cause a yellowing of the substrate.

The components will be preferably dissolved in water, though another medium such as alcohol, acetone, etc., is also possible.

According to a preferred embodiment of the invention, the substrate is treated during the dyeing process. The treatment can be inserted in a continuous as well as well as in a discontinuous dyeing process. When applied in a continuous dyeing process, the treatment can be done before as well as during or after the effective dyeing step. In a discontinuous dyeing process, posttreatment is preferred.

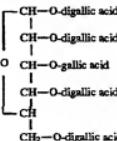
Tannic acid is a compound derived for several centuries from nutgalls and has a structure of polygalloylglucoside or polygalloyquinic acid.

The term "tannic acid" as used in this description and claims should be understood in a broad sense, and covers products containing tannic acid, such as for instance gallotannin.

In fact tannic acid is a mixture of compounds consisting of a glucose-chain which is several times substituted with gallic acid or trihydroxy-3,4,5-benzoic-acid-l. Substitution can also be made with digallic acid or with trigallic acid.

Tannic acid e.g. contains nonagallolylglucose, a glucose-chain substituted 5 times with gallic acid, 4 times of which is digallic acid and the formula of which is the following:

55



According to the invention, any commercial tannic acid can be used, though it is economical to use a tannic acid with

65

a relatively high molecular weight. The molecular weight of the tannic acid will preferably be between 700 and 3500, though this range is not critical.

It has also been found that optimum results can be achieved when the tannic acid component consists of a mixture of a tannic acid with a relatively low MW and a tannic acid with a relatively high MW. So it has been shown that a mixture, consisting of a tannic acid with an average MW lower than 1000 and a tannic acid with an average MW higher than 1500, can give better results than tannic acid of exclusively 1500 MW.

The tannic acid component is preferably used in an aqueous solution. For the man skilled in the art, it will be clear that the water has preferably to be de-ionized and softened.

The solution to be applied will contain 10 to 60 g tannic acid per liter of water, preferably 15 to 25 g/l. To avoid oxidation of the solution, a small quantity of an aliphatic mono carboxylic acid with a boiling-point lower than 100° C., e.g. acetic acid, can be added.

To avoid oxidation of the substrate, it is also recommended to add a non volatile, non hygroscopic and preferably non corroding acid, as e.g. an aliphatic carboxylic acid such as citric acid or polyacrylic acids. It could also be economical to add a wetting agent, such as e.g. isopropanol.

The sulphonic component is a condensation product of a sulphonated phenol- or naphthol-derivate with an aldehyde. Such compounds contain at least a sulphonate group in acid and/or salt form, which is combined with at least a carbon atom of a phenol or naphthol group. The product can be synthesized by reaction of one of these compounds with an aldehyde e.g. formaldehyde. Some of these products and their preparation are described in the above mentioned U.S. Pat. No. 4,501,591. The sulphonic-component, in a concentration of 5 to 50 g/l, can be added to the solution containing the tannic acid component.

It can be advantageous to increase the molecular chain of the components for instance through cross-linking by adding to the solution or to the rinsing water a complexing agent, such as aluminium potassium sulphate or potassium antimonyl tartrate, or a compound reducing the solubility of the sulphon component, such as silicon dioxide gel, a magnesium or zirconium salt, . . . whereby the complexing agent can have a cross-linking effect on the tannic acid and the sulphon component.

The solution containing both components must preferably have a pH between 2.5 and 5, and eventually be adjusted by adding an acid for instance a sulfamic acid, formic acid, citric acid . . . Strong mineral acids have to be avoided.

According to an embodiment of the invention, the substrate to be dyed, will first be treated with the mixture of both components according to the invention and afterwards cold dyed.

The expression "dyed or dyeing" as used in this description means any process by which dyes are applied on a substrate, such as dyeing, printing, spacing, spraying, etc..

The dyes to be applied are dissolved in water, eventually by heating, and afterwards adjusted to the right volume with cold water. The operation will preferably be done in an acid medium.

When applying the dyestuff in a continuous printing process, an acid-resisting thickening agent, such as an hydrocolloide, e.g. Xanthanegum, will preferably be added.

Dyestuffs suitable to be used when applying the mixture according to the invention, are in general acid as well as metalcomplex or disperse dyes. Basic dyestuffs are less suitable, due to the acid conditions.

In case basic dyes are used, it is recommended to apply the treatment according to the invention, as an additional treatment.

Also in a differential dyeing or cross dyeing process, when acid and basic dyes are used, it will be recommended to apply the treatment with the tannic acid- and sulphon-components as an additional operation after dyeing.

For the man skilled in the art, it is obvious to select dyestuffs which fit in the described process and do not cause any side-reactions with the applied reagentia and products.

A good preselection of dyestuffs will be made through obvious criteria. For the process to be followed, it can e.g. be useful to select dyestuffs with fast fixing properties.

Below some dyestuffs that fit in very well in the frame of the invention, are mentioned as non restrictive examples. The dyestuffs are indicated with their corresponding colour index number as it is common practice.

- Acid Yellow 121, 219 and 230
- Acid Orange 116 and 156
- Acid Red 42, 243, 299 and 395
- Acid Blue 40, 113, 129 and 344
- Acid Black 172
- Mordant Orange 6
- Disperse Yellow 2
- Disperse Red 55.1 and 340
- Disperse Blue 7
- Basic Red 23 and 73
- Basic Yellow 45 and 63
- Basic Blue 45 and 129.

Other dyestuffs have also been tested with satisfactory results.

According to another embodiment of the invention, the solution of tannic acid-component and sulphon-component, can also be added directly to the dyebath, so that the substrate can simultaneously both be dyed and treated with the solution according to the invention.

In case of a continuous process, the substrate, after dyeing, is preferably steamed during a half to a few minutes with airfree saturated steam. After steaming, the coloured substrate is rinsed, preferably with cold water, at which a stabilizer can be added, preferably a non volatile, non hygroscopic, and non corroding acid, e.g. an aliphatic carboxylic acid, in a concentration e.g. between 0.5 to 5 g/l.

According to a further embodiment of the invention, the substrate can be dyed following the standard process, and at any time post-treated with the solution according to the invention. In this case the dyed substrate is treated with the solution containing both components, during a few minutes, preferably warmed up to a temperature of $\pm 80^\circ$ C. The treated substrate is then rinsed, steamed and dried following the normal process.

When applied in a discontinuous process, the substrate is preferably dyed according to normal dyeing procedures, and then post-treated in a bath with a solution of tannic acid- and sulphon-components. The bath containing the substrate is preferably gradually warmed up till $\pm 80^\circ$ C. Then the substrate is cooled, rinsed and dried.

It is clear that the improved characteristics can also be obtained by treating a substrate in a two step process, whereby in a first step one of the components (tannic acid-component or sulphon-component) is applied and in a second step the other component, whereby it can be possible to apply for instance the first step before and the second step after dyeing. Such an embodiment needs however an additional treatment.

When a substrate is treated according to one of these embodiments, an unknown resistance to oxidative bleaching

agents and chlorine is noticed. Also an unknown resistance to colour stains of natural or synthetic origin containing anionic, cationic, metalcomplex or disperse dyestuffs, is achieved.

Stains of coffee at 70° C., kool-aid (highly coloured softdrink), wine, ink, etc., can easily be removed by wetting the stain with cold or lukewarm water, and dry dabbing.

An additional advantage of the process according to the invention is, that a coloured substrate shows a better resistance to products such as turpentine and white spirit, and an improved resistance to mildew and house-mite has been observed.

Tests have been executed with respect to light-fastness and washing-fastness, and showed that the process has no influence on the light fastness and a rather positive influence on the washing fastness.

The process and the various ways of applying it is described more in detail below, by way of following non-restrictive examples:

EXAMPLE 1

A solution was prepared by dissolving 10 g tannic acid with a MW of 900 (Mijimoto commercial product) in 10 g/l tannic acid with a MW of 2000 (Mijimoto commercial product) in 1 l of soft water. To this, 25 ml of Alguard NS (Allied Colloids) (40% aqueous solution) was added. Then 2 g of a mixture of polyacrylic acids (Eulyrine S BASF) and 5 ml acetic acid 80% was added as stabilizer, as well as 5 ml isopropanol as wetting agent. The pH of the solution was 2.5.

A piece of substrate (A) consisting of polyamide 6.6 in the form of spun yarns (as used in velvet) was soaked in this solution at room temperature and squeezed till an uptake equal to 100% substrate.

The wet substrate was printed over with Acid Yellow 230. To this end 1 g of dyestuff was dissolved in 0.1 l of warm water, then cold water was added to 1 l. To this solution, 5 ml acetic acid 80% was added, until a pH of 3.5 was obtained. Finally, Xanthan gum Type Kelzan was added until the required viscosity was reached.

After that the substrate was printed, it was steamed with air-free saturated steam at 98° C. during 2 minutes, and then rinsed with cold water. At the rinsing water and/or the last rinsing bath, 2 g of a mixture of polyacrylic acids (Eulyrine S) per liter of water was added. Then the substrate was dried at 100° C.

Comparative 1 a

A piece of substrate (B) from the same material as substrate (A) was dyed with the same dye solution after it has been moistened with an aqueous solution of acetic acid to which isopropanol was added, but without tannic acid or any condensation product of a sulphonated phenol- or naphtol-derivative with an aldehyde. The coloured substrate was steamed and rinsed in the same way as in example 1.

Comparative 1 b

A piece of substrate (C) from the same material as substrate (A) was dyed with the same dye solution after it has been treated with an aqueous solution to which 20 g/l tannic acid, as well as acetic acid and isopropanol was added, but not sulphonated condensation product. The coloured substrate was steamed and rinsed in the same way as in example 1.

Comparative 1 c

A piece of substrate (D) from the same material as substrate (A) was dyed with the same dye solution after it had been moistened with an aqueous solution containing

Alguard NS and additives in the same concentration as in example 1, but without adding tannic acid. The coloured substrate was steamed and rinsed in the same way as in example 1.

5 The substrates were subject to following tests:

Test 1: Benzoylperoxide test

1 cc of a skincare product, Mytolac (Richardson-Vicks), a commercial product containing 5% benzoylperoxide, was spotted on substrates A, B, C and D.

10 The stain was left to dry during 24 hours and then treated with cold water and dabbed dry.

From substrate A, the stain had completely disappeared and there were no traces of any discoloration left.

Substrates B and D were completely discoloured and an orange stain was left.

On substrate C, the stain had disappeared for about 70%, but showed a clear discoloration.

Test 2: Coffee test

A cylinder Ø 4 cm and 40 cm high was placed on the substrate. At the bottom of the cylinder, 10 ml of hot coffee at 70° C was injected, whilst on top of the cylinder a weight of 300 g was dropped to press the coffee into the substrate. This was left untouched during 24 hours.

After 24 hours, the coffee stain was dabbed with hot water (60° C.) and dried up with an absorbing tissue.

The stain on substrate A had completely disappeared.

On substrate B, the treatment had practically no effect on the stain which was only removed for 20%. A further treatment with household bleaching water containing 1 g/l active chlorine was needed to remove the stain. The chlorinated water left a clearly visible pale stain.

On substrate C, the stain was removed for the major part (80%), but a trace remained visible. A further treatment with household bleaching water containing 1 g/l active chlorine was needed to remove the stain. The chlorinated water left a slightly visible pale stain.

On substrate D, the stain was partly removed (45%), but still well visible. A further treatment with household bleaching water containing 1 g/l active chlorine was needed to remove the stain. The chlorinated water left a clearly visible pale stain.

Test 3: Red wine test

With the same testing material as for the test mentioned above, 10 ml of red wine was brought on the substrate and left during 24 hours. Then the stain was treated with lukewarm water and dabbed dry.

The results were similar to those of the coffee test.

On substrate A, the stain was completely removed.

On substrate B, the stain remained visible for 70%.

On substrates C and D, the stain remained visible for 20% to 40%, but a further treatment with chlorinated water was needed, which left a pale stain.

Test 4: Kool-aid test

With the same testing material as for the test 2, a kool-aid stain was made on the substrate. The stain was made with a solution of 95 g/l kool-aid in tap water. After 24 hours the stain was treated with cold water and dabbed dry.

On substrate A, the stain was completely removed.

On substrate B, the stain was still present for 90%.

On substrate C, the stain was still present for 80%.

On substrate D, the stain was almost completely removed.

Test 5: Chlorine test

With a pipette, 2 ml of a solution of respectively 1 g/l, 3 g/l and 10 g/l active chlorine was brought on the substrate.

After 24 hours the stains were visually evaluated.

On substrate A, no discoloration was noticed for 1 g/l and 3 g/l. The solution of 10 g/l had caused a slight discoloration.

On substrate B, there was already a discolouration at 1 g/l. On substrate C, no discolouration was noticed at 1 g/l and 3 g/l. The solution of 10 g/l caused a very clear discolouration.

On substrate D, there was already a discolouration at 1 g/l. It has to be noticed, that a clear difference of discolouration was observed between substrate A and substrate C as of 7 g/l active chlorine.

On substrate B and D a complete discolouration was noticed at 3 g/l and with 10 g/l the substrate was affected.

This test proved that the treatment according to the invention not only protects the colour of the substrate against chlorine, but also gives a protection against the destruction of the substrate itself.

Test 6: Repeated stains

The coffee test (test 2) was repeated several times on the same spot of the substrate, and each time, the stain was treated with lukewarm water.

On substrate A, the coffee stain disappeared after five times (repeated stains) without leaving any trace. When the stain was made on the same spot for the sixth time, there was a slight discolouration visible after treatment with lukewarm water.

Test 7: Light fastness

A part of substrate A was exposed to light according to the DIN norm 54004, corresponding to ISO norm 105/BOZ (Xenoncontest).

The stain resistance test (test 2) as described above, was done on the exposed part after 24 hours of exposure to light, after 48 hours, after 72 hours . . . till after 240 hours of exposure.

The effectiveness of the stain removing treatment was compared with a non exposed part of substrate A. There was no difference noticed between the non exposed and the part exposed to light, even after 240 hours of exposure.

The same test was repeated on substrates A and B and the colour fastness of both substrates was compared after 240 hours of exposure. No colour difference was noticed. Therefore it can be stated that the treatment according to the invention has no influence on the colour fastness.

An additional test showed that for a substrate on the basis of polyamide dyed with a basic dyestuff the light fastness was substantially improved.

Test 8: Shampoo test

A part of substrate A was treated with a neutral carpet shampoo (Belgian Norm NBB: G62-014). The shampoo was mixed with water and the foam brought on the substrate with a brush. The shampoo was left to dry on the carpet and then removed with a vacuum cleaner.

After this treatment, test 2 as described above, was done on the cleaned part and compared to a part of substrate A not treated with shampoo. No substantial difference was noticed. This shampoo treatment did not affect the effectiveness of the stain-removing treatment.

This test was repeated five times, and showed that even after five shampoo treatments, the stain caused by hot coffee, still was completely removable without leaving any traces.

EXAMPLE 2

Example 1 was repeated but on a substrate (E) consisting of polyamide 6 in the form of a bulked continuous filament.

Comparative trials 1a, 1b and 1c were also repeated on substrates (F), (G) and (H), which were identical with substrate (E).

In comparative trial 2a a substrate (F) was treated as in example 2 but without the tannic acid component and without the sulphon component.

In comparative trial 2b a substrate (G) was treated as in example 2 but with the tannic acid component and without the sulphon component.

In comparative trial 2c a substrate (H) was treated as in example 2 but with the sulphon component and without the tannic acid component.

The tests 1 to 4 as given for example 1 were also repeated and the results are summarised in table 1 hereafter. For test 5 only the 3 g/l active chlorine was tested.

EXAMPLE 3

Example 1 was repeated but on a substrate (K) consisting of thermofixed polyamide 6 bulked continuous filament in cut pile.

Comparative trials 3a, 3b and 3c were made on substrates (L) (M) and (N) but:

- (L) without tannic acid component and without sulphon component
- (M) with tannic acid component and without sulphon component
- (N) without tannic acid component and with sulphon component.

The tests 1 to 5 as given for example 1 were also repeated.

EXAMPLE 4

In this example, the treatment according to the invention was applied in a continuous process but after that the substrate has been dyed.

A solution of tannic acid, Alguard NS, polyacrylic acid and acetic acid was prepared in concentrations and compositions as in example 1. The pH of the solution was 3.5.

This solution was poured over a piece of dyed polyamide 6 substrate (P) in the form of a textured continuous filament (as substrate E) and then steamed, rinsed and dried as in example 1.

Comparative trials 4a, 4b, 4c

Pieces of substrate (Q), (R), (S) from the same material as substrate (P) were post-treated with the same solution, but respectively:

- (Q) without tannic acid and without Alguard NS
- (R) without Alguard NS but with tannic acid
- (S) without tannic acid but with Alguard NS.

The tests 1 to 5 as given for example 1 were repeated.

EXAMPLE 5

In this example, the substrate was dyed in a discontinuous process, and afterwards treated with the solution according to the invention.

A piece of polyamide 6.6 substrate (T) in the form as substrate A (example 1) was dyed in the classic way with an acid dyestuff and rinsed. Thereafter the substrate was immersed in a bath containing a solution of tannic acid, Alguard NS, and polyacrylic acid in concentrations and with composition as in example 1.

The bath was gradually heated till 80° C. and kept at this temperature for about 20 minutes, then cooled, rinsed and dried.

Comparative trials 5a, 5b, 5c

Pieces of substrate (U), (V), (W) from the same material as substrate (T) were dyed in the same way, but respectively treated:

- (U) without tannic acid and without Alguard NS
- (V) without Alguard NS but with tannic acid
- (W) without tannic acid but with Alguard NS.

The tests 1 to 5 as given for example 1 were repeated.

TABLE I

Substrate	1	2	3	4	5
A	0	100	100	100	0
B	100	20	30	10	100
C	30	80	80	20	0
D	100	60	60	95	100
E	0	100	100	100	0
F	100	20	30	30	100
G	25	95	95	60	0
H	100	30	30	100	100
K	0	100	100	100	10
L	100	20	30	30	100
M	33	70	90	50	30
N	100	30	30	100	100
P	0	100	100	100	0
Q	100	20	30	30	100
R	30	90	90	50	0
S	100	30	30	100	100
T	0	100	100	100	0
U	0	20	30	20	100
V	30	70	90	50	0
W	100	30	30	95	100

Test 1 Benzoylperoxide test % discoloration

Test 2 Coffee test % of stain disappeared

Test 3 Red wine test % of stain disappeared

Test 4 Kool-aid test % of stain disappeared

Test 5 Chlorine test % discoloration with 3 g active chlorine per liter.

It is obvious that the invention is not restricted to the described examples, but applies for any process by which a substrate is treated with a tannic acid solution (whereby tannic acid is to be understood in a broad sense, as described hereabove) and a solution containing a condensation product of a sulphonated phenol- or naphthol-derivative with an aldehyde. This treatment can be done before, during or after dyeing.

The examples were intentionally given with an identical mixture of tannic acid and Alguard NS, so that results could be better compared.

Additionally to the described tests, laboratory tests were made with coloured stains originating from different types of drinks and all results confirmed the improved resistance.

Furthermore tests were made with a tannic acid from other suppliers and did not show any difference, so that any available commercial product can be used. The molecular weight however is an important factor, and it can be preferred to use a mixture of tannic acid with a low MW, and a tannic acid with a high MW.

Tests were also carried out with different other condensation products of a sulphonated phenol- or naphthol-derivative with aldehydes, with equal results.

Instead of Alguard NS, different Mesitol (Bayer) products, different Stainmaster (Du Pont de Nemours) products, Erional KF (Ciba), Matexil FA-SNX (Zeneca), Resist 80-20 (Sandoz), Intratex N (Crompton & Knowles), etc., can also be used.

The examples were given with use of different polyamide substrates to demonstrate the results on the different characteristics of the fibres. As a matter of fact each polyamide has its own characteristics. So is PA 6 different from PA 6.6, is a PA with a continuous filament different from a PA with fibres in a spun yarn and that there are differences resulting from the manufacturing process, for instance PA thermofixed or not thermofixed.

The method is described and illustrated on the hand of polyamide fibres, but can be used for a large range of other substrates such as wool, silk, cotton, cellulose substrate as well as polyester, polypropylene, polycrylonitrile fibres, modified or not, in the form of polymers as well as in the

form of copolymers or bicomponent synthetic fibres. Tests made on various fibres confirmed the positive results.

It is clear that the treatment with the solution containing tannic acid and a condensation product of a sulphonated phenol- or naphthol- derivative with an aldehyde, can be combined with other compounds used in the field of the textile industry to seek for additional properties.

The concentrations, temperatures and reaction times were determined by the man skilled in the art, according to the used reagent, products, dyestuffs, production process, type of substrate, etc...

Also the choice of stabilizer, wetting agent and other auxiliaries will be made by the man skilled in the art, who will take care that the selected auxiliaries do not cause any undesired reaction with the tannic acid component or the sulphur component or with any other product used.

I claim:

1. Method for improving the stain resistance of a substrate made out of dyed or dyeable natural or synthetic fibres, said method comprising contacting the substrate in acid medium with tannic acid and with sulphonated phenol- or naphthol-aldehyde condensation product, the amounts of tannic acid and sulphonated product each being in the range of 10 to 90 percent, based on the total weight of said tannic acid and sulphonated product, and producing improved stain resistance in said substrate through such contacting.

2. Method according to claim 1, wherein the total weight of said tannic acid and sulphonated product represents 1 to 6% by weight of said medium.

3. Method according to claim 1, wherein the amounts of tannic acid and sulphonated product are in the ranges of 40 to 80% and 20 to 60% respectively, based on the total weight of said tannic acid and sulphonated product.

4. Method according to claim 3, wherein the total weight of said tannic acid and sulphonated product represents 1 to 6% by weight of said medium.

5. Method according to claim 1, wherein the acid medium is an aqueous solution having a pH in the range of 2.5 to 5.

6. Method according to claim 1, 2, 3, 4 or 5 wherein the tannic acid has a molecular weight equal to or greater than 1500.

7. Method according to claim 1, 2, 3, 4 or 5 wherein the tannic acid is a mixture of tannic acid with a molecular weight lower than 1000 and tannic acid with a molecular weight higher than 1500.

8. Method according to claim 1, wherein the substrate is brought into contact with the tannic acid and sulphonated product before, during or after dyeing of the substrate.

9. Method according to claim 1, wherein the substrate is brought into contact with the tannic acid and sulphonated product during dyeing of the substrate.

10. Method according to claim 1, wherein the substrate is brought into contact with the tannic acid and sulphonated product after dyeing of the substrate.

11. Method according to claim 1 wherein the medium is an aqueous solution and contains a stabilizer in an amount sufficient to avoid oxidation of the substrate and the solution.

12. Method according to claim 1, wherein the tannic acid and sulphonated product are brought into contact with the substrate sequentially.

13. A substrate of natural or synthetic fibers having improved stain resistance as compared to that of the untreated substrate, said substrate having been

(a) treated with tannic acid and sulfonated phenol- or naphthol-aldehyde condensation product, in amounts sufficient to improve the stain resistance of the substrate; and

(b) colored by application of dyestuff prior to, during or after treatment of the substrate with said tannic acid and sulphonated product.

14. A substrate with improved stain resistance as compared to that of the untreated substrate, said substrate of improved stain resistance being a product of the process of treating a substrate made of dyed or dyeable natural or synthetic fibres, in acid medium, with tannic acid and with sulphonated phenol- or naphthol-aldehyde condensation product, the amounts of tannic acid and sulphonated product each being in the range of 10 to 90 percent, based on the total weight of said tannic acid and sulphonated product.

15. A substrate according to claim 13 or 14 which comprises polyamide fibre.

16. A substrate according to claim 13 or 14 which is in the form of carpet.

17. An improved method of cleaning a colored substrate, wherein the improvement comprises:

pretreating said colored substrate, in an acidic medium prior to the presence of a given stain on said substrate, 20 with tannic acid and sulphonated phenol- or naphthol-aldehyde condensation product, the amounts of tannic acid and sulphonated product each being in the range of 10 to 90 percent based on the total weight of said tannic acid and sulphonated product; and

cleaning said stain from the pretreated substrate.

18. Method according to claim 17 wherein said substrate is cleaned by application of water to the stain.

19. Method according to claim 17 or 18 wherein the stain is composed of a persistent dye or pigment selected from among coffee, tea, wine, fruit juice or ink. 30

5 20. A solution for improving the stain resistance of a substrate, said solution containing tannic acid and sulphonated phenol- or naphthol-aldehyde condensation product, the amounts of tannic acid and sulphonated product each being in the range of 10 to 90 percent, based on the total weight of said tannic acid and sulphonated product.

10 21. A solution according to claim 20 wherein the amount of tannic acid is in the range of 40-90%, based on the total weight of said tannic acid and sulphonated product.

22. Method for producing a colored substrate of natural or synthetic fibres having improved stain resistance, said method comprising

(a) contacting the substrate with tannic acid and sulphonated phenol- or naphthol-aldehyde condensation product at a combined weight concentration of 1-6% in aqueous acid medium, the amounts of tannic acid and sulphonated product each being in the range of 10 to 90 percent, based on the total weight of said tannic acid and sulphonated product, the total of said amounts being sufficient to improve the stain resistance of the substrate.

(b) coloring said substrate with dye applied during or after contacting said substrate with said tannic acid and sulphonated product, and

(c) recovering a product of improved stain resistance as compared to a similarly dyed product not contacted with said tannic acid and sulphonated product.

* * * * *

United States Patent

[19]

Gamblin

[11] Patent Number:

4,842,646

[45] Date of Patent:

Jun. 27, 1989

[54] SUBSTANTIVE DYES, INKS AND DYE
BATHS

[75] Inventor: Rodger L. Gamblin, Dayton, Ohio

[73] Assignee: Saranda Consolidated Limited
Partnership, Dayton, Ohio

[21] Appl. No.: 910,653

[22] Filed: Sep. 23, 1986

[51] Int. Cl.⁴ C09D 11/00[52] U.S. Cl. 106/22; 106/20;
8/527; 8/594[58] Field of Search 106/20, 22; 8/636, 527,
8/919, 594, 595, 644, 649

[56] References Cited

U.S. PATENT DOCUMENTS

590,139 9/1897 Dunlap .
1,787,233 12/1930 Bivins 106/271,905,347 4/1933 Dreyfus 106/20
2,022,413 11/1935 Ellis et al 8/5
4,101,329 7/1978 Lock 106/22
4,156,657 5/1979 Lyn 106/22
4,159,203 6/1979 Lock 106/22
4,421,561 12/1983 Brinkus 106/20
4,624,709 11/1986 Atsuthi 106/22*Primary Examiner—Josephine Barr
Attorney, Agent, or Firm—Donald E. Degling*

[37] ABSTRACT

A dye composition comprising (a) a water insoluble nigrosine dye, induline dye or basic dye, (b) a water miscible solvent, and (c) a hydroxycarboxylic acid having at least three hydroxy groups is useful in preparing aqueous inks and dye baths. If desired, such baths may also include a mordant, a humectant and a corrosion inhibitor.

17 Claims, No Drawings

SUBSTANTIVE DYES, INKS AND DYE BATHS

The present invention relates to dyes, inks and dye baths and to methods of preparing and using such dyes, inks and dye baths. The dyes, inks and dye baths of the present invention are aqueous solutions or are soluble in aqueous solutions and are thus conveniently used. Nevertheless, they are substantive on cellulose and commonly used textiles (e.g., textiles manufactured from wool, silk, cotton, and acrylonitrile), as well as on papers, so that they may be used to obtain a permanent mark or color. The dyes, inks and dye baths of the present invention may be used with equipment that has metal or plastic parts because the compositions of the present invention tend to have a low degree of aggression toward such parts. The dyes of the present invention may be used in textile dyeing, flexographic printing of newspapers and packaging, and in the preparation of ink-jets inks and writing instrument inks.

Nigrosine and induline dyes may be prepared as the hydrochloride and as such are soluble in lower alcohols (i.e., they are spirit soluble) but are insoluble in water. These dyes may be sulfonated with sulfuric acid so as to make them water soluble. Whereas spirit soluble nigrosine and induline dyes, if used in a non-aqueous solvent (e.g., a dye bath comprising methanol, ethanol, or a glycol), are capable of permanently marking substrates such as cellulose, wood, and the like, sulfonated nigrosine and induline dyes have little affinity for many such substrates and will readily wash off upon exposure to water.

This lack of substantivity of sulfonated nigrosine and induline dyes, coupled with the inconvenience of using the more substantive spirit soluble dyes (which require an alcoholic solvent rather than water), has resulted in the textile industry and the printing industry not making substantial use of such dyes. This is unfortunate because such dyes are relatively inexpensive, have high tintorial strength, and are relatively stable.

Water is readily available, very inexpensive and non-toxic. As a result, it is, by far the most widely used medium for the application of dyes in the textile industry and it is used as a solvent for inks whenever practical. Most papers are made so as to yield non-feathering marks with aqueous inks. Thus, flexographic and gravure printing system inks and rolling writer and fiber tip pen inks yield a sharp image with water based vehicles on such papers. Therefore, it is desirable that a dyestuff intended to be used in the textile industry or in one of the aforementioned inks be water soluble.

I have found that I can make nigrosine dyes, induline dyes, and water insoluble basic dyes soluble in water without causing them to lose their substantivity on various substrates (e.g., cellulose, silk, and wool). The dyes that may be solubilized include both the aforementioned dyes and the corresponding dye bases. Accordingly, as used herein, and unless indicated otherwise, the terms nigrosine dye, induline dye or basic dye shall be understood to include both the dye and the corresponding dye base.

In the method of my invention, solubilization of a dye in an aqueous solution is achieved by reacting the dye, dissolved in a water miscible solvent, with a hydroxycarboxylic acid containing multiple hydroxy groups. While I do not wish to be bound by any theory, I believe that such hydroxycarboxylic acids are able to solubilize a dye by forming a complex with the dye

cation that is similar to a chelate. A chelate generally comprises one or more polydentate ligands and a metal ion. The interaction between the ligand and the metal ion results in a modification of the solution properties (e.g., solubility) of the metal ion. While I do not wish to be bound by theory, I believe that in a composition of my invention, the hydroxycarboxylic acid is acting as a polydentate ligand and the dye cation is acting as if it were a metal ion. The complex that results from the interaction between the hydroxycarboxylic acid and the dye cation unexpectedly is substantive upon cellulose or clay-coated substrates (e.g., claycoated paper) but has a low degree of aggression toward the metal components of printing equipment.

Many basic dyes (for example, Crystal Violet, Rhodamine B, Auramine O, Victoria Pure Blue BO, Basic Blue 1, and Basic Blue 3) are more or less water soluble and have little or no substantivity for cellulose or similar materials. Such dyes can, however, be rendered water insoluble by treating them with one or two times their own weight of an insolubilizing agent such as tannic acid or gallic acid. Other insolubilizing agents (also known as mordants) such as Tamolan A Liquid (a proprietary replacement for tannic acid, manufactured by BASF Wyandotte Corporation of Parsippany, N.J.) may also be used to render basic dyes water insoluble. It has long been known that organic acids such as acetic, citric, tartaric, formic, ethyl tartaric or glycolic acid and solvents such as acetone (the monoethylester of glycerine) are useful in maintaining at least some solubility of basic dye in the presence of tannic acid (see for example, E. Knecht & J. Forthergill, *Principles and Practices of Textile Printing*, Second Edition, pages 288-295, J. B. Lippincott Company, Philadelphia, Pa. (1924)). I have found, however, that the use of such organic acids is not desirable because the resulting solutions generally form precipitates within a day or two (See Example 15). Thus, the use of such solutions for dyeing and printing is limited to solutions that are freshly prepared. Such solutions, however, would not be suitable when used for inks or for dye baths intended to be used over a period of time, since the precipitation would prevent proper dyeing of the substrate. On the other hand, without using such acids, combinations of water soluble basic dyes with insolubilizing agents such as tannic acid and gallic acid generally cannot be applied from an aqueous bath since the combinations are insoluble in water. In order to avoid this problem, one would treat a cellulose substrate with an insolubilizing agent such as tannic acid, then subject the treated substrate, after drying, to a dye bath, and finally treat the dyed material with an aqueous solution of tartar emetic. Thereafter, the fabric would be washed and dried. Alternatively, the dye and the insolubilizing agent might be solubilized in a lower alcohol (e.g., methanol, ethanol or isopropanol) and used in an alcoholic vehicle.

I have found that by properly treating combinations of dye and tannic acid with the hydroxycarboxylic acids of the present invention, I can obtain a water soluble system that can conveniently be used to directly dye cellulose materials, wool, silk, or acrylonitrile fabric from a single aqueous dye bath. The fabric so treated is permanently dyed and may be washed in water or put through a washing machine without substantial loss of color. Similarly, paper may be permanently dyed or printed with such compositions and the dye will not bleed off even if the paper is immersed in water.

As used herein, and unless indicated otherwise, the term "water insoluble" as applied to a nigrosine dye, an induline dye or a basic dye, means a dye that by itself or in the presence of a mordant (because it has been pretreated with a mordant (e.g., tannic acid or gallic acid) or because of the solution in which it is to be dissolved contains a mordant (e.g., tannic acid or gallic acid)) is insoluble or is soluble to an extent of no more than 1 mg./liter of water but that can be solubilized with the aid of a hydroxycarboxylic acid so that it is soluble in an aqueous solution of the present invention to an extent of at least about 150 mg. of dye per milliliter of solution.

In one of its embodiments, the present invention relates to a dye composition comprising

- (a) a water insoluble nigrosine dye, induline dye or basic dye;
- (b) a water miscible solvent; and
- (c) a hydroxycarboxylic acid having at least three hydroxy groups.

The foregoing composition may be diluted with water to prepare an aqueous solution.

The present invention also relates to an ink or dye bath comprising an aqueous solution that comprises

- (a) a water insoluble nigrosine dye, induline dye or basic dye;
- (b) a water miscible solvent;
- (c) a hydroxycarboxylic acid having at least three hydroxy groups; and
- (d) water.

As will be discussed in greater detail below, the foregoing solution may be prepared by combining the dye, the water miscible solvent and the hydroxycarboxylic acid and then adding water. Alternatively, the first two components and a portion of the third component may be combined and the resulting solution may be diluted with an aqueous solution containing the balance of the hydroxycarboxylic acid. Additional ingredients, such as a humectant, a corrosion inhibitor, or both, may also be added to the inks and dye baths of the present invention.

A preferred embodiment of the present invention relates to an aqueous ink or dye bath comprising

- (a) a water insoluble nigrosine dye, induline dye or basic dye;
- (b) a water miscible solvent;
- (c) a hydroxycarboxylic acid having at least three hydroxy groups;
- (d) a mordant (e.g., tannic acid or gallic acid, preferably tannic acid); and
- (e) water.

The foregoing ink or dye bath may also contain a corrosion inhibitor, humectant or both.

A particularly preferred embodiment of the present invention relates to an aqueous ink or dye bath comprising

- (a) about 0.0001 to about 15 parts by weight of a water insoluble nigrosine dye, induline dye or basic dye;
- (b) about 0.0001 to about 60 parts by weight of a hydroxycarboxylic acid having at least three hydroxy groups;
- (c) about 0.0001 to about 60 parts by weight of a water miscible solvent;
- (d) about 25 to about 100 parts by weight of water; and optionally,
- (e) about 0.0001 to about 30 parts by weight of a mordant (e.g., tannic acid or gallic acid, preferably tannic acid).

The foregoing ink or dye bath may also contain a corrosion inhibitor, a humectant or both.

In the dye compositions, inks and dye baths of the present invention the weight ratio of said hydroxycarboxylic acid to said water insoluble nigrosine dye, induline dye or basic dye is preferably in the range of about 4 to 1 to about 0.5 to 1, more preferably about 2.1 to about 1 to 1, and most preferably about 1 to 1. However, for dyes that are difficult to dissolve, the use of a hydroxycarboxylic acid to dye weight ratio greater than 1 to 1, and in exceptional cases greater than 4 to 1, may be desirable. In such compositions, the concentration of hydroxycarboxylic acid in the aqueous inks and dye baths of the present invention generally ranges up to about 20 percent by weight (based on the weight of the solution) and is preferably no more than about 15 percent by weight, and more preferably no more than about 10 percent by weight.

Nigrosine and induline dyes are azine dyes. Their character and preparation are described in more detail in, for example, Vol. A3 of *Ullman's Encyclopedia of Industrial Chemistry*, (VCH Publishers, Deerfield Beach, Fla., 1985). A nigrosine dye may be made by heating a mixture of aniline, nitrobenzene, hydrochloric acid, and iron slowly to a temperature of a little over 200° C. Subsequent to the heating process, the dye is powdered and slurried first with dilute hydrochloric acid and then with a dilute aqueous solution of sodium carbonate to first remove any excess aniline and then to convert the dye to the dye base form. The resulting material is sold as a dry powder to users and is called nigrosine base or C.I. (Color Index) Solvent Black 7 (C.I. Number 50415). Other nigrosine dyes are similarly prepared.

If a spirit or alcohol soluble nigrosine dye is desired, the aforementioned washing with dilute sodium carbonate solution is eliminated. If a water soluble nigrosine dye is desired, it may be prepared by heating nigrosine base to about 110° C. with three times its weight in sulfuric acid until a test sample of the reaction product becomes soluble in dilute ammonium hydroxide. The dye is then washed and neutralized with sodium hydroxide.

An induline dye may be made by heating a mixture of aniline, aniline hydrochloride, and phenylazoaoline to a temperature near 180° C. The melt is ground and washed in a weakly basic solution to form the dye base. The dye base is sold as a powder and is referred to as C.I. Solvent Blue 7 (C.I. Number 50400). Other induline dyes are similarly prepared.

Dyes related to indulines but of different shades (ranging from bluish reds to deep blues) may be made by reacting together (a) an aromatic amine having its para position free, (b) the hydrochloride of the foregoing amine and (c) an aromatic amine that is substituted at its para position with a substituted or unsubstituted phenyl or naphthyl azo group. Most such materials are water insoluble though some diamine compounds have a degree of solubility (but many may be insoluble when combined with a mordant). As used herein, unless indicated otherwise, the words "induline dyes" should be understood to include the foregoing dyes that are related to indulines.

There are large numbers of basic dyes that were initially prepared prior to the 1960's. Within the last twenty years, in response to the discovery that many basic dyes are lightfast on polyacrylonitrile, a number of new basic dyes have been prepared (e.g., by the

diazocoupling of sulfur-containing heterocyclic compounds to aromatic amines). Generally, basic dyes are brilliantly colored and have a high tinctorial strength. Basic dyes, by definition, carry a positive charge and are also called cationic dyes since they are attracted in solution to the negative electrode or cathode of an electrochemical cell. Basic dyes that are useful in the present invention include: Malachite Green, Basic Blue 1, Basic Blue 3, Basic Blue 41, Rhodamine B, Rhodamine 6G, Basic Yellow 11, Auramine O, Thioflavine T, Acridine Orange, Auramine G, Basic Red 12, 14, or 15, Basic Violet 16, Acridine Yellow, Crystal Violet, Basic Orange 21, Methyl Violet, Ethyl Violet, and Victoria Pure Blue BO. I have chosen to consider dyes such as Solvent Blue 23 (which is insoluble even in the absence of a mordant) basic dyes since they carry a positive charge in an acidic solution of a solvent in which they are soluble (e.g., methanol). Although I have referred to nigrosine or induline dyes as separate groups of dyes in discussing the dye component in my invention, nigrosine or induline dyes may also be considered basic dyes because they also carry a positive charge in an acidic solution in which they are soluble.

Basic dyes vary widely in solubility. Some such as Rhodamine B are readily soluble in water (but are insoluble when combined with a mordant) while others such as Victoria Blue B have poor solubility in water.

As used herein, and unless indicated otherwise, the term "a hydroxycarboxylic acid having at least three hydroxy groups" shall be understood to mean a hydroxycarboxylic acid having at least three hydroxy groups, not including the hydroxy group that is part of the carboxyl group and not including a hydroxy group that is a substituent on an aromatic ring. Preferably, each required hydroxy group is a substituent on an aliphatic carbon atom. It will also be understood that the hydroxycarboxylic acid should be soluble in the aqueous solutions of the present invention. Glucuronic acid is the most readily available of the hydroxycarboxylic acids that are useful in the compositions of the present invention and is, therefore, preferred. Other hydroxycarboxylic acids that may be used include α -D-glucopyranose acid gamma-lactone, galactonic acid, and glucuronic acid. Other useful hydroxycarboxylic acids may be prepared by oxidizing sugars such as fructose, mannitol, galactose, and the like to the corresponding acids or by oxidizing similar carbohydrates to the corresponding acids. Such oxidation may be performed with bromine or nitric acid under mild conditions, for example, by warming an aqueous solution of the sugar with nitric acid. A mixture of hydroxycarboxylic acids rather than a single hydroxycarboxylic acid may be used in the compositions of the present invention and the term "hydroxycarboxylic acid having at least three hydroxy groups" shall be understood to include such mixtures. Such mixtures may be obtained, for example, by the oxidation of corn syrup.

The water miscible solvent used to prepare the dye compositions, inks and dye baths of the present invention should be capable of dissolving the nigrosine dye, induline dye or basic dye with which it is to be used and should be capable of forming a solution with water. Preferably, the solvent should not excessively attack (e.g., cause corrosion or swelling of) the metal or plastic parts used in printing and dyeing equipment. Suitable solvents include alcohols, such as methanol, ethanol, and isopropanol, glycols, such as ethylene glycol, diethylene glycol, polyethylene glycol, 1,3-butandiol, hex-

ylene glycol, glycol DB, and glycol DE, dimethylformamide, N-methyl-2-pyrrolidine, and dimethylsulfoxide. Methanol and dimethyl formamide are preferred solvents.

A mordant is not always required for all inks or dye baths of the present invention simply because some dyes (e.g., nigrosine dyes, induline dyes, Solvent Blue 23, and Violazime) are not water soluble and thus will not readily be washed off with water. Nevertheless, most common basic dyes require a mordant when they are used to dye fibers such as silk or cotton or are used in inks for printing upon paper. Although certain dyes may not always require a mordant, the fastness of such dyes (e.g., Solvent Blue 23) may be improved if a mordant is used. Tannic acid is especially useful in fixing some dyes (e.g., Solvent Blue 23) and making them fast to washing. When a mordant is used in the dye compositions, inks and dye baths of the present invention, the amount of mordant is preferably in the range of about 2 to 1 parts by weight of mordant for each part by weight of dye or dye base.

Tannic acid is readily available and relatively inexpensive and is, therefore, a preferred mordant. Other mordants may be prepared by reacting formaldehyde with phenol or salicylic acid or by reacting sulfur with phenols. Most such mordants are proprietary materials and, generally, their structures are not known. Tamolan A (available from BASF), discussed above, may be a reaction product of sulphur and phenol. Other fixing agents similar to tannic acid (e.g., gallic acid) may also be used. Such agents have been widely discussed in the literature. See, for example K. Venkataraman, *The Chemistry of Synthetic Dyes*, Vol. I, page 278, Academic Press, New York, New York (1952). Combinations of mordants (e.g., combinations of tannic acid and Tamolan A) may also be used as the mordant in the compositions of my invention.

I have found that when tannic acid is used to insolubilize a basic dye, the resulting material may generally be used to prepare solutions that are compositions of the present invention. However, combinations of Tamolan A and basic dyes are not always sufficiently solubilized by the hydroxycarboxylic acids of my invention. For example, combinations of Crystal Violet and Tamolan A are generally solubilized by the hydroxycarboxylic acids of my invention but combinations of Malachite Green and Tamolan A are not solubilized by said hydroxycarboxylic acids. Accordingly, as used herein and unless otherwise indicated, the term mordant, as applied to the compositions of my invention, shall be understood to mean an insolubilizing agent that combines with a basic dye to yield an insoluble material that may be resolubilized using a hydroxycarboxylic acid having at least three hydroxy groups. Whether a particular insolubilizing agent is considered a mordant of the present invention depends upon the basic dye that is used together with the insolubilizing agent. If the combination of the dye and the insolubilizing agent can be resolubilized with a hydroxycarboxylic acid having at least three hydroxy groups, the insolubilizing agent is considered a mordant of the present invention. On the other hand, if the aforementioned combination cannot be resolubilized with a hydroxycarboxylic acid having at least three hydroxy groups, the insolubilizing agent is not considered a mordant of the present invention.

The most common metallic materials found in printing presses, ink jet systems, writing instruments and textile dyeing systems are stainless steel, copper, brass,

nickel and steel. Although the compositions of the present invention tend to have a low degree of aggression toward these materials, it is preferred to further protect these materials by the addition of a corrosion inhibitor. It is generally not necessary, however, to further protect the plastic components of printing, writing or dyeing equipment from the compositions of the present invention.

Compositions comprising benzotriazole and, optionally, also comprising copper sulfate are preferred corrosion inhibitors. Benzotriazole is compatible with the dye systems described below in Examples 1-14, is readily available, and inhibits corrosion without staining metal parts. Mercaptobenzothiazole is also useful as a corrosion inhibitor, either by itself or in combination with copper sulfate.

Other useful corrosion inhibitors are compositions comprising benzothiazole or mercaptobenzothiazole and a salt selected from the group consisting of stannous sulfate, other stannous salts, copper salts other than copper sulfate, and silver salts.

The optimum amount of corrosion inhibitor for a particular application will depend on variables such as the specific hydroxycarboxylic acid used, its concentration, and the pH of the solution. When a combination of benzotriazole and copper sulfate is used as the corrosion inhibitor, the concentration of benzotriazole is generally about 2.2 to about 0.5% by weight based on the weight of the solution and the concentration of the copper sulfate is about 50 parts by weight per million parts by weight of solution.

A composition of the present invention that comprises about 10% by weight of gluconic acid can generally be inhibited against corrosion of copper by as little as about 0.2% by weight (based on the weight of the solution) of benzotriazole or a few parts per million by weight (based on the weight of the solution) of mercaptobenzothiazole. A composition of the present invention that comprises about 10% by weight gluconic acid can generally be inhibited against corrosion of iron by a few parts per million by weight of copper sulfate (based on the weight of the solution) in conjunction with about 0.5% by weight (based on the weight of the solution) of benzotriazole.

For ink jet inks, a small amount of humectant (e.g., on the order of about 1 to about 2%), such as ethylene glycol, diethylene glycol, other glycols, sorbitol, glycercin, and the like is generally added in order to maintain or prevent drying out of the ink, whereas with pen-inks the humectant content is generally on the order of about 15 to about 30%.

A general procedure for preparing water soluble versions of insoluble nigrosines, indulines or basic dyes is to add the dye or dye base (generally, use of the dye base is preferable in order to avoid the presence of chloride ion which would enhance the tendency of the solution to cause corrosion) to a water miscible solvent, add an agent or agents that serve(s) as a mordant (e.g., tannic acid), if required, and then add an appropriate amount of hydroxycarboxylic acid, as discussed above. The hydroxycarboxylic acid may be added as a solid or it may be added as an aqueous solution. Preferably, the hydroxycarboxylic acid is added as a solution that is 50% by weight hydroxycarboxylic acid. Such solutions where the hydroxycarboxylic acid is gluconic acid are commercially available. The weight of water miscible solvent usually is at least twice the weight of the dye and preferably is about 5 to about 10 times the weight of

the dye. Reaction may occur at room temperature or gentle heating (up to about 40° C.) for a period of a few minutes may be required. Generally, the resulting solution will be completely soluble in water or it will at least be soluble in a solution that comprises up to about 10% by weight (based on the weight of the solution) of hydroxycarboxylic acid (e.g., gluconic acid). Use of such a 10% by weight solution of hydroxycarboxylic acid may be necessary in preparing an ink or dye bath comprising a very difficult to dissolve combination of dye and mordant (e.g., a combination of Tamolan A and tannic acid with a relatively water insoluble dye). When diluting the aforementioned resulting solution, it is preferable to add diluent slowly (especially when diluting with water rather than with a 10% solution of hydroxycarboxylic acid) so as not to cause precipitation of dye, particularly when the dye is one that is difficult to dissolve.

The amount of aqueous solution that should be added to the solution of dye, acid, water miscible solvent and mordant to prepare an ink or dye bath depends upon the desired concentration of dye in such ink or dye bath. Factors to be considered include the tintorial strength of the dye, the shade of dyed fabric desired, and, for inks, the required thickness of the ink film. For an ink jet ink, the final concentration of the dye is generally in the range of about 0.1% to about 1% by weight (based on the weight of the ink), whereas for a newspaper ink, generally, the dye (e.g., nigrosine) content is between about 2 and about 15% by weight (based on the weight of the ink) and for a writing instrument ink, about 2 to about 7% by weight (based on the weight of the ink). For textile dyeing, depending upon the shade desired and the tintorial strength of the dye, the amount of dye in a dye bath can range from about 0.0001% to as much as about 3% by weight, based on the weight of the dye bath solution.

The following non-limiting Examples 1-14 illustrate the preparation of compositions of the present invention. Example 15 is a comparative Example. Unless indicated otherwise, the materials used in the Examples were technical grade.

EXAMPLES

EXAMPLE 1

Several aqueous solutions were prepared by dissolving a dye or dye base in a water miscible solvent (e.g., methanol), adding a hydroxycarboxylic acid, warming the mixture and then diluting with water. The amount of water used to dilute the mixture was dependent upon the intended use (e.g., dye bath, ink jet ink, newspaper ink, or writing instrument ink). In all cases, however, at least 50 ml of water was used. In some cases, a mordant was added to the methanol before adding the hydroxycarboxylic acid solution. The amounts of materials used, other than water, are shown in Table I.

Using this method, the following dyes have been solubilized:

(a) roseinduline, a rose colored dye prepared by reacting phenylazo-1-naphthylamine with 1-naphthylamine, aniline, or a mixture of aniline and 1-naphthylamine. This dye has the same structure as C.I. Number 50370, but is not sulfonated.

(b) a brilliant violet dye prepared by reacting 4-(orthochloro)orthochloroaniline with ortho-

chloroaniline at 180° C. This dye is not listed in the Color Index.

(c) a green dye prepared by reacting trichlorotoluene with diphenylamine in the presence of zinc chloride (C.I. Number 42125 is prepared by sulfonating this dye);
 (d) 95% Neptune Blue Base NB652, obtained from BASF Wyandotte, Parsippany, N.J. (C.I. Number 42760, Solvent Blue 23), which may be made by reacting aniline with rosaniline in the presence of benzoic acid at about 200° C.;
 (e) a purple dye prepared by reacting pararosaniline with aniline in the presence of benzoic acid (C.I. Number 42795 is prepared by sulfonating this dye);
 (f) Spirit Fast Violet R (C.I. Number 45185) prepared by condensing ortho-toluidine with 3,6-dichlorofuran in the presence of zinc chloride; and
 (g) Violamine 3G Spirit Soluble (C.I. Number 45195), a violet dye prepared by condensing 2,6-xyldine with 3,6-dichlorofuran in the presence of zinc chloride.

Solvent Blue 23 exhibits good lightfastness and will not stain wool when used to dye wool polyacrylonitrile blends. Generally, I have found that the anilino type derivatives described above not only exhibit at least as 25 brilliant a shade as the more common basic dye but also exhibit greater light fastness than the basic dye. For example, the anilino, orthotoluidino and 2,6-xyldino derivatives of Rhodamine B generally exhibit light fastness at least 2 AAATCC (American Association Of Textile Colorists And Chemists) scale ratings beyond that of the parent basic dye on cotton.

TABLE I

DYE OR DYE BASE	SOLVENT	HYDROCARBOXYLIC ACID	TEMPERATURE OF SOLUTION	TIME OF REACTION	MORDANT
1. 10 grams of nigrosine base ^a	50 ml methanol	10 ml of 50% aqueous solution of glucosin acid ^d	25° C.	5 min.	None
2. 5 grams of Malachite Green base ^b	100 ml methanol	10 ml of 50% aqueous solution of glucosin acid ^d	40° C.	10 min.	10 grams of tannic acid ^d
3. 5 grams of Baso Red, NB 546 ^c	100 ml methanol	10 ml of 50% aqueous solution of glucosin acid ^d	40° C.	5 min.	10 grams of tannic acid ^d
4. 5 grams of Neptune Blue base, NB 652 ^c	100 ml methanol	10 ml of 50% aqueous solution of glucosin acid ^d	25° C.	5 min.	None
5. 10 grams of nigrosine base ^d	100 ml methanol	10 grams of α-D-glucopyranose acid γ-lactone ^d	25° C.	10 min.	None

^aOrient Chemical Corp., Newark, New Jersey^bDye Specialties, Secaucus, New Jersey^cBASF Wyandotte, Parsippany, New Jersey^dAldrich Chemical Co., Milwaukee, Wisconsin^eGem City Chemicals Inc., Dayton, Ohio

EXAMPLE 2

50 grams of Crystal Violet from Dye Specialties Incorporated, Secaucus, N.J., were added to 500 ml of methanol, with stirring. Thereafter, 50 grams of tannic acid (obtained from Mallinckrodt, Inc., St. Louis, Mo.) and 100 ml of a 50% aqueous solution of gluconic acid (solution obtained from Gem City Chemicals Inc. Dayton, Ohio) were added, with stirring. This mixture was diluted with a 10% aqueous solution of gluconic acid to give a dye bath that dyes cotton or silk in beautiful purple shades. The amount of dilution may be varied depending upon the desired depth of shade on the dyed fabric. This dye bath is suitable for dyeing cellulosic materials, silks, and polyacrylonitriles.

EXAMPLES 3-6

Substitute 50 grams Auramine O, 50 grams Rhodamine B, 50 grams Basic Blue 1, or 50 grams Victoria Pure Blue BO for the Crystal Violet, in order to prepare respectively yellow, magenta, blue-green, and pure blue dyes. These materials can be mixed to form various shadings.

EXAMPLE 7

In order to prepare an ink for a writing instrument, two grams of Crystal Violet were added to 10 grams of dimethylformamide and 10 grams of triethylene glycol, with stirring. With continued stirring, 2 grams of tannic acid were then added, followed by 20 grams of a 50% aqueous solution of gluconic acid. The resulting solution was then diluted with 60 grams of water and 0.2 gram of benzotriazole and 5×10^{-3} gram of copper sulfate were then added.

EXAMPLES 8-10

Substitute the following amounts of dyes and amounts of tannic acid for the Crystal Violet and tannic acid in Example 7 to obtain beautiful red, blue and green inks in Examples 8, 9 and 10, respectively:

EXAMPLE	DYE	TANNIC ACID
8	2 grams Rhodamine B; 1 gram Auramine O	3 grams
9	2 grams Victoria Pure Blue BO; 0.5 gram Crystal Violet	3 grams

55	10	2 grams Basic Blue 1;	4 grams
----	----	-----------------------	---------

EXAMPLE 11

60 10 grams of nigrosine base (obtained from Orient Chemical Corp.) were slurried with 40 milliliters of methanol. To this mixture, a 50% solution of gluconic acid (solution from Gem City Chemicals Inc.) was added. Very shortly thereafter, the dye became totally soluble upon dilution with 450 ml of water and could be passed through a 0.7 micron filter. The resulting solution was used to dye silk, cotton, linen, jute and acrylonitrile and gave substantive dyes that after drying would not bleed off.

EXAMPLE 12

A dyestuff made according to the method of Example 11 was diluted with water so that the bath contained approximately 1% nigrosine. A textile dipped for one minute in the bath and dried at room temperature was dyed completely substantively in a beautiful gray/black color. The weakly acidic bath appeared to have no harmful effects upon the fabric.

EXAMPLE 13

In order to prepare an ink jet ink, 10 grams of nigrosine base (obtained from Orient Chemical Corp.) were dissolved in 60 grams of ethylene glycol with the aid of 12 grams of a solution of 50% by weight gluconic acid in water and 1 gram of benzotriazole. The resulting solution was diluted with 440 grams of water and filtered. This system, though completely soluble and compatible with an ink jet printer, imparted a permanent black OCR scannable mark to cellulose and clay coated paper substrates.

EXAMPLE 14

A writing instrument ink was made by dissolving 6 grams of nigrosine base (obtained from Orient Chemical Corp.) along with 5×10^{-3} gram of copper and 0.2 gram of benzotriazole in a solution of 10 grams of dimethylformamide and 10 grams of triethylene glycol with the aid of 7.2 grams of a 50% by weight solution of gluconic acid in water to form an ink that gives a permanent intense black mark upon writing papers when used with rolling writer or fiber tip pens.

EXAMPLE 15

In order to evaluate the suitability of organic acids for solubilizing dyes in the presence of tannic acid, I have taken one part by weight of a dye, and mixed the dye with two parts by weight of tannic acid in five parts by weight of methanol. I then added three parts by weight of an organic acid. After gentle warming for a few minutes, I then diluted the mixture with 200 parts by weight of water. This procedure was followed for each of the following dyes: Rhodamine B, Auramine O, Basic Blue 1, Crystal Violet, Victoria Pure Blue BO, Victoria Blue R, Victoria Blue B, Basic Blue 3, Malachite Green, Methyl Violet, Ethyl Violet, Basic Yellow 11, Basic Yellow 28, nigrosine and indulin. The suitability of each of the following acids was evaluated as described above: acetic, citric, tartaric, formic, maleic, glycolic, and lactic acid.

With the exception of the methanol solutions of tannic acid and Victoria Blue B, nigrosine or indulin, which formed precipitates immediately upon the addition of most of the foregoing organic acids, the dye-tannic acid mixtures appeared to be soluble in organic acids and did not precipitate when the solution was diluted with water. However, after a period of time ranging from a few minutes to a day or two, precipitation was observed.

I claim:

1. A dye comprising

(a) about 0.0001 to about 15 parts by weight of a solubilized water insoluble nigrosine dye, indulin dye or basic dye;

- (b) about 0.0001 to about 60 parts by weight of a water miscible solvent; and
- (c) about 0.0001 to about 60 parts by weight of a hydroxycarboxylic acid having at least three hydroxy groups and not more than six hydroxy groups.
- 2. A dye according to claim 1, wherein the hydroxycarboxylic acid is gluconic acid.
- 3. An ink or dye bath comprising an aqueous solution 10 that comprises:
 - (a) about 0.0001 to about 15 parts by weight of a solubilized water insoluble nigrosine dye, indulin dye or basic dye;
 - (b) about 0.0001 to about 60 parts by weight of a water miscible solvent;
 - (c) about 0.0001 to about 60 parts by weight of a hydroxycarboxylic acid having at least three hydroxy groups and not more than six hydroxy groups; and
 - (d) about 25 to about 100 parts by weight of water.
- 4. An ink or dye bath according to claim 3, wherein the hydroxycarboxylic acid is gluconic acid.
- 5. An ink or dye bath according to claim 3, wherein the weight ratio of said hydroxycarboxylic acid to said water insoluble nigrosine dye, indulin dye or basic dye is in the range of about 4 to 1 to about 0.5 to 1.
- 6. An ink or dye bath according to claim 5, wherein said ratio is about 1 to 1.
- 7. An ink or dye bath according to claim 3, said ink or dye bath comprising
 - (a) a water insoluble nigrosine dye, indulin dye or basic dye;
 - (b) a water miscible solvent;
 - (c) a hydroxycarboxylic acid having at least three hydroxy groups;
 - (d) a mordant; and
 - (e) water.
- 8. An ink or dye bath according to claim 7, wherein the mordant is selected from the group consisting of tannic acid and gallic acid.
- 9. An ink or dye bath according to claim 7, wherein the hydroxycarboxylic acid is gluconic acid.
- 10. An ink or dye bath according to claim 7, said ink or dye bath also comprising a humectant.
- 11. An ink or dye bath according to claim 7, said ink or dye bath also comprising at least one corrosion inhibitor.
- 12. An ink or dye bath according to claim 7, wherein the weight ratio of said hydroxycarboxylic acid to said water insoluble nigrosine dye, indulin dye or basic dye is in the range of about 4 to 1 to about 0.5 to 1.
- 13. An ink or dye bath according to claim 12, wherein said ratio is about 1 to 1.
- 14. An ink or dye bath according to claim 7, said ink or dye bath also comprising about 0.0001 to about 30 parts by weight of a mordant.
- 15. An ink or dye bath according to claim 14, wherein the mordant is selected from the group consisting tannic acid and gallic acid.
- 16. An ink or dye bath according to claim 15, wherein the hydroxycarboxylic acid is gluconic acid.
- 17. An ink or dye bath according to claim 14, wherein the hydroxycarboxylic acid is gluconic acid.

United States Patent [19]**Fekete**[11] **4,094,701**[45] **June 13, 1978****[54] METHOD FOR CLEANING TIN SURFACES****[75] Inventor:** Douglas D. Fekete, Warren, Mich.**[73] Assignee:** Oxy Metal Industries Corporation,
Warren, Mich.**[21] Appl. No.:** 668,011**[22] Filed:** Mar. 18, 1976**[51] Int. Cl.²** B08B 3/08
[52] U.S. Cl. 134/2; 134/40;

252/84; 252/85

[58] Field of Search 134/2, 29, 40; 252/84,
252/85, 156**[56] References Cited****U.S. PATENT DOCUMENTS**

1,628,163	5/1927	Lillejord	252/84
2,215,814	9/1940	Hall	252/85 X
2,836,566	5/1958	Duncan	134/2 X

3,888,783 6/1975 Rodzewich 134/2 X

FOREIGN PATENT DOCUMENTS

28,863	2/1931	Australia	252/84
19,292 of	1907	United Kingdom	252/85
1,293,440	10/1972	United Kingdom	252/84

Primary Examiner—S. Leon Bashore*Assistant Examiner*—Marc L. Caroff*Attorney, Agent, or Firm*—Arthur E. Kluegel; Bertram F. Claeboe; Richard P. Mueller**[57] ABSTRACT**

An aqueous alkaline solution containing an organic tannin is used to clean a tin surface. The composition is particularly useful for cleaning tin surfaces because the presence of the tannin inhibits etching of the tin surface which normally occurs under alkaline conditions.

5 Claims, No Drawings

METHOD FOR CLEANING TIN SURFACES

BACKGROUND OF THE INVENTION

This invention relates to the art of cleaning a substrate surface. In particular, it relates to the art of cleaning, without at the same time etching, a tin surface. Even more particularly, it relates to the art of cleaning tin-plated surfaces, such as tin cans which have been previously subjected to cold forming operations during which organic lubricants are applied to the tin surface as drawing aids.

Cleaning is essential as a preliminary to many surface finishing operations. Cleaning is normally required, for example, prior to corrosion preventive treatments and prior to the application of organic finishes to the surface. Cleaning is especially important in the case of metal surfaces to which organic materials have been recently applied as an aid to cold forming, which materials must then be removed in order to obtain a surface 15 suitably receptive to an organic finish.

One example of the need for such a cleaner is in the manufacture of two piece, tin-plate, drawn and ironed cans. In the manufacture of tin-plate cans, circular blanks of tin-plated steel are first cupped and then passed through several drawing dies to iron the cup in order to form a unitary side wall and can bottom structure. These forming operations are assisted and the dies and metallic surface protected by the application of 20 lubricants to the tin-plate surface prior to or during the forming operation. Since it is desired to have a clean surface in order to assure adhesion of a subsequently applied sanitary lacquer and/or decorative varnish, the cleaning step after forming is critical to a successful manufacturing process.

Conventional cleaners for metal surfaces are described in the *Metal Finishing Guidebook and Directory*, pages 195-218, (1974). Cleaners useful for tin-plate surfaces are described, for example, by R. J. Kerr in *J. Soc. Chem. Ind. (London)* 65:101 (1946). The Kerr article refers to alkaline aqueous composition for tin-plate cleaning containing sodium dichromate, trisodium phosphate, and sodium hydroxide.

Difficulties with tin surface cleaners have centered around an attempt to obtain a cleaner which will provide a waterbreak-free surface without unduly etching the surface. Etching results from chemical attack of the tin surface which roughens and dulls the surface. Alkaline cleaners have been found most suitable for producing the desired clean surface, but have been less than desirable because of their tendency to etch the surface. Where a smooth, shiny surface is desired such as in the case of a beverage can, etching is clearly undesirable. Furthermore, etching removes a portion of the corrosion protective tin from the surface thereby degrading the anti-corrosion qualities of the surface. It has previously been discovered that the presence of hexavalent chromium compounds in the cleaning solution will help to inhibit etching of the tin surface under the alkaline conditions employed. The use of chromium compounds is undesirable however because they are environmentally objectionable in plant effluents and because they are highly toxic and therefore of concern when used in connection with the processing of food containers such as beverage cans.

It would therefore be desirable to have available an alkaline aqueous cleaning composition which could be used to clean substrate surfaces, but which when em-

ployed to clean a tin surface will not cause undue etching.

SUMMARY OF THE INVENTION

It has now been discovered that the inclusion of an organic tannin component in an aqueous alkaline cleaning composition will inhibit etching of a tin surface by the alkaline cleaner. Thus, the cleaner of the present invention has the advantage that it may be used to clean a variety of surfaces either simultaneously or sequentially without necessitating resort to a special separate cleaner when it is desired to clean a tin surface.

DETAILED DESCRIPTION OF THE INVENTION

The cleaner of the present invention is an alkaline aqueous composition. One or more surfactants will normally be employed to further the cleaning ability of the cleaner and an organic tannin component is included to inhibit etching of tin surfaces.

The specific alkaline component employed in the cleaning composition is not critical. Any compounds normally employed to provide alkalinity in an aqueous cleaner are suitable. Examples include the alkali metal borates, carbonates, phosphates, hydroxides, oxides and silicates. These components should be present in the solution in concentrations sufficient to provide a cleaner of the desired pH.

The chemistry of organic tannins is not completely understood. The organic tannins include natural extracts and synthetic materials. Extracts include a large group of water soluble, complex organic compounds widely distributed throughout the vegetable kingdom. All have the common property of precipitating gelatin from solutions and of combining with collagen and other protein matter in hides to form leather. All natural tannin extracts examined contain mixtures of polyphenolic substances and normally have associated with them certain sugars. (It is not known whether these sugars are an integral part of the structure.) For a discussion of tannins, see *Encyclopedia of Chemical Technology*, 2nd edition, Kirk-Othmer; XII (1967) pages 303-341 and *The Chemistry and Technology of Leather*, Reinhold Publishing Corporation, New York, pages 98-220 (1958).

Tannins are generally characterized as polyphenolic substances having molecular weights of from about 400 to about 3000. They may be classified as "hydrolyzable" or "condensed" depending upon whether the product of hydrolysis in boiling mineral acid is soluble or insoluble, respectively. Often extracts are mixed and contain both hydrolyzable and condensed forms. No two tannin extracts are exactly alike. Principal sources of tannin extracts include bark such as wattle, mangrove, oak, eucalyptus, hemlock, pine larch, and willow; woods such as quebracho, chestnut, oak and urunday, cutch and turkish; fruits such as myrobalans, valonia, divi-divi, tara, and algarrobia; leaves such as sumac and gambier; and roots such as canaire and palmetto.

The term "organic tannins" is employed to distinguish natural extract and synthetic organic tannins such as those listed in the previous paragraph from the mineral tanning materials such as those containing chromium, zirconium and the like. Experimental work has shown that hydrolyzable, condensed, and mixed varieties of organic tannins may all be suitably used in the present invention.

The concentration of the organic tannin in the cleaner must be of at least such minimum amount as to inhibit etching of a tin surface. The precise minimum concentration required will depend to some extent upon the temperature and pH of the particular cleaner employed. Normally, a concentration of at least 0.01% or greater will be required. Concentrations as high as the solubility limit of the solution may be employed, but should not be required.

Examples of tannins which may be employed in the present invention are listed in Table I. The preferred tannins are myrobalan, wattle, tannic acid, quebracho, and chestnut extract.

An added advantage of the presence of tannin is that corrosion resistance as measured by ASTM Salt Spray 15 and Humidity tests is improved over that obtained with the same cleaner without the tannin.

The temperature and pH of the cleaning solution are interrelated. Increased temperatures as well as increased pH values tend to improve the cleaning rate of the cleaner. Whereas a temperature of 125° F might be suitable at a pH value of 12.5, a temperature of 150° F may be required to obtain the same results at a pH of 10.3. In general, the pH of the cleaner should be at least 9.0 and is preferably between 10 and 13. Most preferably the pH of the cleaner is between 10 and 10.5. The presence of the organic tannin inhibits etch even at high pH values, but it has been found that the higher pH values tend to gradually inactivate the tannin necessitating more frequent additives. Accordingly, the lower pH values in the alkaline range are preferred because they favor stability of the tannin. Thus, temperatures of 140° F and upwards will normally be employed when the cleaner is adjusted to the preferred pH range.

The temperature employed will normally be a function of the selected pH value of the cleaner. Temperatures of from 100° to 180° F may be suitable with temperatures in excess of 140° F being desirable for the preferred pH range.

The presence of one or more surfactant compounds in an alkaline aqueous cleaner solution often acts as an aid to the cleaning power of the solution. The presence or absence of surfactants has been found to have no noticeable effect as far as

TABLE I

TANNINS NAME	SUPPLIER
Tannic Acid	Merck and Company, Inc.
Tannic Acid (Tech. 10)	S.B. Penick and Company
Tannic Acid (Tech. 3C)	The Harshaw Chemical Co.
Tannic Acid (Tech. XXX)	The Harshaw Chemical Co.
Tannic Acid (Tech. 7c)	The Mead Corporation
Chestnut Extract	Arthur C. Trask Corp.
Spray Dried Chestnut	Arthur C. Trask Corp.
Bleached Quebracho	Arthur C. Trask Corp.
Extract	Arthur C. Trask Corp.
Non-Bisulfited	Arthur C. Trask Corp.
Quebracho Extract	Arthur C. Trask Corp.
Wattle Extract	Arthur C. Trask Corp.
Chest Extract	Arthur C. Trask Corp.
Myrobalan Extract	Arthur C. Trask Corp.

inhibiting or promoting the etching of a tin surface by the cleaner. If desired, any surfactant known to be useful for alkaline aqueous cleaners may be employed in the cleaner of the present invention. Specific examples 65 include Triton N101 manufactured by Rohm & Haas Co. which is a nonyl phenoxy polyethoxy ethanol; Tergitol 15-S-9 manufactured by Union Carbide Corp.

which is a polyethylene glycol ether of a linear alcohol; Pluronic 31-R-1 manufactured by BASF Wyandotte Corp. which is a condensate of propylene oxide, ethylene oxide and ethylene glycol; and Tergitol 08 manufactured by Union Carbide Corp. which is a sodium sulfate derivative of 2-ethyl-1-hexanol.

The cleaner of the invention is particularly suitable for cleaning tin-plate surfaces and also functions to satisfactorily clean the surfaces of other substrates and in particular other metal substrates such as steel and aluminum.

EXAMPLE 1

Drawn and ironed tin-plate can bodies were spray cleaned with an aqueous solution containing:

Component	wt. %
Na ₂ CO ₃	0.25
NaOH	0.15
Tannin (Myrobalan)	0.05
Triton N101	0.05
Pluronic 31-R-1	0.025

The pH value of the cleaner was 12.5 and the temperature was 125° F. The cans were waterbreak-free after 1.5 minutes, but exhibited no etch even after 3 minutes contact.

EXAMPLE 1A

Cleaning as in Example 1 at a temperature of 140° F resulted in unetched waterbreak-free cans after one minute.

EXAMPLE 1B

Cleaning as in Example 1 with a myrobalan content of 0.025% resulted in unetched waterbreak-free cans after one minute.

EXAMPLE 1C

The concentrations of Example 1 were doubled giving a pH value of 13.0. At 130° F unetched waterbreak-free tin cans were obtained after 1.5 minutes.

EXAMPLE 1D

Cleaning as in Example 1 with 0.025% Wattle substituted as the tannin resulted in unetched waterbreak-free tin cans after one minute.

EXAMPLE 1E

Cleaning as in Example 1A with 0.05% of Tergitol 08 substituted for the two surfactants resulted in unetched waterbreak-free tin cans after 2 minutes. Many other surfactants were substituted with similar results.

EXAMPLE 1F

To simulate a used cleaning bath, 0.01% of Quakerol 539, a water emulsifiable lubricant commonly employed in can forming, was added to the cleaner of Example 1. Unetched waterbreak-free tin cans were obtained at 140° F after 1.5 minutes.

COMPARATIVE EXAMPLE 1

Example 1 was repeated, but the tannin was omitted from the cleaner. After only 1 minute at 125° F the tin surface had been visibly attacked and was frosted in appearance.

EXAMPLE 2

An aqueous cleaner was prepared to contain:

Component	wt. %
Na ₂ HPO ₄	0.26
Na ₃ PO ₄	0.16
NaOH	0.37
Tannin (Myrobalan)	0.036
Tergitol 15-S-9	0.016
Triton NI01	0.010
Pluronic 31-R-1	0.026

At a pH of 12.4 and a temperature of 125° F, unetched waterbreak-free tin cans were obtained after 2 minute spray.

EXAMPLE 3

An aqueous cleaner was prepared to contain:

Component	wt. %
Na ₂ CO ₃	0.26
NaOH	0.26
Tannin (Tannic Acid)	0.026
Tergitol 15-S-9	0.095
Triton NI01	0.063

At a pH of 11.8, unetched, waterbreak-free tin cans were obtained after 1 minute spray at temperatures of 130° to 150° F.

EXAMPLE 3A

Example 3 was repeated with 0.026% Quebracho substitute for the tannin. At a pH of 12.1, unetched waterbreak-free tin cans were obtained after 1 minute spray at temperatures of 130° to 140° F.

EXAMPLE 4

An aqueous cleaner was prepared to contain:

5

At a pH of 12.5, unetched, waterbreak-free tin cans 10 were obtained at 130° F after 1.5 minutes. No etching was observed even after 3 minutes.

EXAMPLE 5

An aqueous cleaner was prepared to contain:

Component	wt. %
Tannin (Wattle)	0.033
Triton NI01	0.066
Pluronic 31-R-1	0.033
Potassium Phosphate	to pH 10.3

At a temperature of 150° F, unetched waterbreak-free tin cans were obtained after 1 minute.

What is claimed is:

- 25 1. A process for cleaning a tin surface without substantial etching thereof comprising contacting the surface with an aqueous alkaline solution having a pH value of at least 9.0 and containing an organic tannin in an amount sufficient to inhibit etching of the surface.
- 30 2. The process of claim 1 wherein the tannin concentration of the solution is at least 0.01 wt. %.
3. The process of claim 1 wherein the solution is maintained at a temperature of 100° to 180° F.
4. The process of claim 1 wherein the solution pH value is between 10 and 13.
- 35 5. The process of claim 1 wherein the solution additionally contains a surfactant in an amount sufficient to improve the cleaning ability of the solution.

40

45

50

55

60

65



US005520962A

United States Patent [19]

Jones, Jr.

[11] Patent Number: 5,520,962

[45] Date of Patent: May 28, 1996

[54] METHOD AND COMPOSITION FOR
INCREASING REPELLENCY ON CARPET
AND CARPET YARN

0268374A2 5/1988 European Pat. Off.
0328822A2 8/1989 European Pat. Off.
032989A2 8/1989 European Pat. Off.

OTHER PUBLICATIONS

[75] Inventor: Dennis J. Jones, Jr., Dalton, Ga.
[73] Assignee: Shaw Industries, Inc., Dalton, Ga.
[21] Appl. No.: 388,033
[22] Filed: Feb. 13, 1995
[51] Int. Cl. 5 B05D 3/02
[52] U.S. Cl. 427/393.4; 8/115.56; 8/115.64;
427/430.1; 428/96; 524/539; 524/544; 524/599;
524/805
[58] Field of Search 8/115.51, 115.54,
8/115.6, 115.56, 115.64; 427/393.4, 430.1;
428/96; 524/539, 544, 599, 805

Greschler, Imrich, "Stain-Resistant Polyamide Fibers with Resistance to Yellowing by Nitrogen Dioxide", *Chemical Abstracts*, vol. 108, No. 2, 1988, p. 72.

Jose, D. J., "Stain Resistant Carpets", *Textile Journal*, Nov. 1988.

Liss, Theodore Arthur, "Stain and Yellowing-Resistant Polyamide Fabrics", *Chemical Abstracts*, vol. 108, No. 6, Feb. 1988, p. 86.

Shima, Tsukasa, "Antistatic, Stain-Resistant Polyester Textiles", *Chemical Abstracts*, vol. 81, Jul. 1974, p. 72.

Anton, Anthony, "Polyamide Fiber Reactive Chemical Treatments For Differential Dyeability", —, vol. 13, No. 2, 1981, pp. 31-35.

Carr, J., "Nylon and the Carpet Industry", *Textile Horizons*, Jun. 1988, pp. 43-45.

Lipson, M., "Use of Polymers to Immunize Wool Against Acid Dyes", *Nature*, Jun. 1, 1946, vol. 57.

"Leukatex Acrylic Syntans Product Summary", *Rohm and Haas Leather Chemicals*, Rohm and Haas Company, 1985.

Porter, Raymond, "Acrylic Syntans For Retanning Leather", *Leather*, Sep. 1969, pp. 93-95, 101.

Shortland, F. J. D., "The Role of Acrylics in Wet Processing", *Journal of the Society of Leather Technologists and Chemists*, vol. 64, No. 3, May-Jun. 1980, p. 60.

"Leukatex 970 Acrylic Syntan", *Rohm and Haas Leather Chemicals*, Rohm and Haas Company, 1984.

"Retan 540", *Rohm and Haas Leather Chemicals*, Rohm and Haas Company, 1981.

*Primary Examiner—Michael Lusignan
Attorney, Agent, or Firm—William Brinks Hofer Gilson & Lione*

ABSTRACT

The invention is directed to a method and composition for treating carpet yarn and carpet to thereby enhance its repellency, and preferably to enhance its stain resistance as well. In one aspect of the invention, the method includes the steps of providing a carpet yarn comprising polymeric fibers. An anionic or nonionic fluorocarbon compound is provided in an aqueous medium, the aqueous medium having a pH below about 3.5. The carpet yarn is immersed in the aqueous medium. The carpet yarn and aqueous medium are heated after which excess water is removed from the carpet yarn. The aqueous medium preferably also includes an anionic binding compound that acts to impart stain resistance to the yarn.

References Cited

U.S. PATENT DOCUMENTS

1,901,536	3/1933 Schafer	52B/150
1,972,754	9/1934 Biedermann	52B/150
1,988,985	1/1935 Schaefer	52B/150
2,036,161	3/1936 Schutte	52B/150
2,112,361	3/1938 Fischer	52B/150
2,171,808	9/1939 Russell et al.	52B/150
2,581,390	1/1952 Groot	52S/502
3,221,079	11/1965 Harris	52B/150
3,433,666	3/1969 Moyse	117/139.5
3,650,801	3/1972 Hinton, Jr. et al.	117/47 A
3,824,125	7/1974 Hinton, Jr. et al.	849/116
3,843,576	10/1974 Parkinson	260/29.3
3,849,162	11/1974 Meuller et al.	8/156
3,949,124	4/1976 Illia	428/96
4,501,591	2/1983 Ucci et al.	8/495
4,592,940	6/1986 Blyth et al.	428/96
4,680,212	7/1987 Blyth et al.	428/97
4,780,080	10/1988 Greschler et al.	8/115.6
4,822,373	4/1989 Olson et al.	8/115.6
4,839,212	6/1989 Blyth et al.	428/96
4,857,392	8/1989 Kirjanov et al.	428/267
4,865,885	9/1989 Herlant et al.	427/532
4,875,903	10/1989 Payet et al.	8/115.56
4,877,538	10/1989 Kirjanov et al.	252/8.7
4,937,123	6/1990 Chang et al.	8/115.6 X
5,073,442	12/1991 Knowlton et al.	428/267
5,084,306	1/1992 McLellan et al.	427/393.4
5,219,620	6/1993 Potter et al.	427/434.2
5,310,828	5/1994 Williams et al.	8/115.51 X
5,366,161	11/1994 Potter et al.	239/455

FOREIGN PATENT DOCUMENTS

0235980A1	9/1987	European Pat. Off.
0267681A2	5/1988	European Pat. Off.

METHOD AND COMPOSITION FOR
INCREASING REPELLENCY ON CARPET
AND CARPET YARN

BACKGROUND OF THE INVENTION

The present invention relates to the field of carpet manufacture, and more particularly relates to methods of treating carpet or carpet yarn to enhance its repellency and, preferably, to enhance its stain resistance also.

In the last two decades, there has been considerable interest in developing treatments for carpet fibers, particularly nylon carpet fibers, to enhance repellency and stain resistance. For example, it is now a common practice to topically apply a compound from the class known as fluorochemicals. The object of applying such fluorochemicals is to reduce the tendency of soil, oil and/or water to adhere to the carpet fibers. In addition to soil, the fluorochemicals can also reduce the tendency of oil and/or water to adhere to the carpet fibers. It is also a common practice to apply a stain resist compound to nylon carpet to make the nylon carpet fibers resistant to staining, particularly by anionic or "acid" dyes. The mechanism for stain resist compounds is believed to involve blocking of the dye sites on the nylon polymer.

The fluorochemicals include a fluorinated component, typically a perfluoroalkyl chain, and a nonfluorinated backbone. The nonfluorinated backbone can take a variety of configurations. The important feature of the backbone is that it is capable of forming durable film on the surface of the carpet fiber.

As to the mechanism of soil repellency, it is believed that the attraction between nonpolar soil and the fiber surface is governed by London dispersion forces. Applying fluorochemicals to the surface is thus believed to be effective because the polarizability of perfluoroalkyl chains is lower than that of the hydrocarbons, amines, or carbonyls otherwise found on the surface of a nylon carpet fiber.

Generally, fluorochemicals are topically applied to carpet. One method is to form an aqueous dispersion of the fluorochemical and then spray that dispersion on the top face of the carpet. Another method is to make an aqueous based foam containing the fluorochemical and then apply the foam to the top face of the carpet. Heat is usually applied to drive off excess water and to fix the fluorochemical to the carpet fibers.

Typically, stain resist compounds are applied to carpet from a bath after the dyeing step, but before drying. At least one system is commercially available wherein a fluorochemical and stain resist compound are topically applied in a foam. In particular, the FX-1367F fluorochemical composition and the FX-668F stain resist composition, both from 3M Specialty Chemicals Division, are recommended to be topically co-applied in a foam. The pH of the combined foam is about 4.

SUMMARY OF THE INVENTION

In accordance with one aspect, the invention is a method of treating carpet yarn to enhance its repellency which includes providing a carpet yarn made from polymeric fibers and providing in an aqueous medium with a pH below about 3.5 and a repellency compound comprising an anionic or nonionic fluorochemical. The carpet yarn is contacted with this aqueous medium. The carpet yarn and aqueous medium are preferably heated, after which excess water is removed from the carpet.

In accordance with another aspect of the invention, the aqueous medium further comprises an anionic polymer binding compound, such as a polymer of methacrylic acid.

In accordance with yet another aspect, the invention is a composition for treating carpet to enhance its repellency and stain resistance which includes an aqueous medium, a repellency compound comprising a fluorochemical, and an anionic polymer stain resist compound.

One advantage of the preferred embodiment of the present invention is that it provides a more efficient method of applying fluorochemical and stain resist compound. In particular, since both fluorochemical and stain resist compound are applied in a single bath, the processing, energy and equipment costs are greatly reduced.

Another advantage of the preferred embodiment of the invention is that, as will be shown below, superior repellency results are achieved through the simultaneous application. It is believed that one reason for this improvement is that the present invention provides better penetration of the fluorochemical into the carpet yarn than is achieved through a topical application.

As used herein, the term repellency is intended to have a relatively broad meaning, referring to a reduced tendency for soil, oil and/or water to adhere to the carpet fibers.

As used herein, the term stain resistance is also intended to have a relatively broad meaning, referring to a reduced tendency of the carpet fibers to be stained by acid dyes and/or disperse dyes.

When percentages are given, unless otherwise indicated, they are intended to refer to percentages by weight solids based on the total weight of the aqueous dispersion.

The present invention, together with attendant objects and advantages, will be best understood with reference to the detailed description below.

DETAILED DESCRIPTION OF THE
PREFERRED EMBODIMENTS

Various types of carpet yarn can be treated according to the present invention. Preferably, the method is used to treat carpet, namely carpet yarn tufted into a backing material. Alternatively, the carpet yarn can be treated according to the method before it is tufted into carpet.

Typically, the carpet yarn will be made from an extruded synthetic polymer, such as nylon, polyester or polypropylene. Alternatively, the carpet yarn can be made from a natural fiber, such as wool or cotton. Preferably, the carpet yarn is made from extruded fibers of nylon 6, nylon 6,6, polyester and polypropylene. In the aspect of the invention when both a repellency and a stain resist compound are simultaneously applied, the carpet yarn is most preferably made from either nylon 6 or nylon 6,6. In another aspect of the invention, the yarn is preferably made from polypropylene. The present invention has been found to be particularly advantageous in treating polypropylene carpet in that it provides a cost-effective way of increasing the repellency of polypropylene.

The extruded fibers can be made into yarn by various means. Most preferably, the nylon yarn is a bulk continuous filament yarn which is heat set by conventional means, such as the Superba or the Suesen method. Alternatively, the yarn can be a staple spun yarn. Also, it is preferred that the yarn is not pre-treated with a fluorochemical by the yarn manufacturer.

As noted above, it is preferred that the carpet yarn has already been tufted by conventional means into a carpet

structure before being treated by the present invention. Neither the stitch pattern nor the density appear to be critical to the practice of the invention. Also, if the carpet is to receive a dye treatment, such as application of an acid dye, it is preferred to complete that dye treatment before treating it by the present invention.

The invention employs an aqueous medium comprising a fluorochemical compound. The fluorochemical compound can be an anionic or nonionic fluorochemical. Also, the fluorochemical can be either the telomer type or the electrochemically fluorinated fluorochemical referred to above. Several commercially available fluorochemical compounds have been shown to work in the method of the present invention. Suitable fluorochemical compounds include the following: FX-1367F and FX-1355 both from 3M Specialty Chemicals Division, NRD-372 from DuPont Flooring Systems, TG-232D from Advanced Polymers, Inc., and Nuba 3555 from Hoechst Celanese. All of these commercially available fluorochemical compositions have been successfully applied through the method of the present invention. Currently, the NRD-372 from DuPont is most preferred.

The level of fluorochemical in the medium will be set so as to produce the desired level on the carpet yarn. Preferably, the fluorochemical is present between about 0.0035 and about 0.175 percent solids of the medium. More preferably, the fluorochemical is present at between about 0.015 and about 0.080 percent, most preferably, about 0.02 percent.

An important feature of the aqueous dispersion is that it has a pH of below about 3.5 when the carpet yarn or carpet is immersed in it. This pH is lower than the pH of conventional fluorochemical compositions applied to carpets. Nevertheless, it is believed that the lower pH helps drive the fluorochemical out of solution and onto the carpet yarn fibers. Preferably, the pH of the dispersion is above about 1.0 and below about 3.5, more preferably, between about 1.5 and about 1.8.

This pH can be obtained by adding the appropriate amount of an acid, such as urea sulfate or sulfamic acid, to the aqueous dispersion.

Preferably, the aqueous dispersion also includes an anionic binding compound. More preferably, this anionic binding compound is one that also serves as a stain resist compound, although this function is not required. For example, when the carpet yarn is made from polypropylene, there are no acid dye sites for the anionic binding polymer compound to block. Nevertheless, it has been found that the use of the anionic polymer binding compound has improved the performance of the fluorochemical compound on polypropylene carpet yarn. While not wishing to be bound by any particular theory, it is currently believed that the anionic polymer functions to hold the fluorochemical to the surface of the fiber.

Several anionic polymer binding compounds that also function as stain resist compounds on nylon carpet yarn have been found to work well in the present invention. The preferred anionic polymer binder compounds are polymers or copolymers of methacrylic acid. Preferably, these polymers or copolymers have a molecular weight range such that the lower 90 weight percent has a weight average molecular weight in the range of about 2500 to 250,000 and a number average molecular weight in the range of 500 to 20,000.

Currently, the most preferred anionic polymer binding compound is a polymethacrylic acid commercially available from Rohm & Haas under the designation Leukotan 1028. The molecular weight of the lower 90 weight percent based on weight average for Leukotan 1028 is reported to be 9,460 and based on number average is reported to be 5,592.

Currently, the second most preferred anionic polymer binding compound is a polymer of methacrylic acid designated XP-4-49 which is made according to the procedure described in the examples below. Preferably, the XP-4-49 is mixed with a lesser amount of a phenolic type stain resist compound sold by Sybron Chemicals, Inc. the designation "Tanatex Stainfree." The preferred ratio of XP-4-49 to Tanatex is about 18:1 based on solids. This particular mixture is designated XP-4-50 in the examples below and is the second most preferred anionic polymer binding/stain resist compound to use in the method of the present invention.

Other anionic polymer binding/stain resist compounds have also been shown to work well. The following compositions from 3M Specialty Chemicals Division have worked well: FX-369, FX-668F, FX-661, and FX-657. The principal ingredient of FX-369 is believed to be a phenolic resin. All of the other 3M stain resist compositions are believed to comprise a methacrylic acid polymer or copolymer and to be described in either U.S. Pat. Nos. 4,937,123; 4,822,373 or both.

The composition sold by DuPont Flooring Systems as "SR 300" has also shown good results in the invention. SR 300 is a proprietary composition with a phenolic resin as the principal ingredient.

In addition to the Leukotan 1028 referred to above, other Leukotan compounds from Rohm & Haas have shown promise, namely 1027, 970 and 1084. With the exception of the Leukotan 1084, the Leukotans are all polymers and copolymers of methacrylic acid of varying molecular weights. Although these compounds are generally sold to the tanning industry, U.S. Pat. No. 4,937,123 refers to this group as having stain resist properties when applied to nylon carpet fibers. Leukotan 1084 is believed to be a polymer of acrylic acid.

Preferably, the anionic binding/stain resist compound is present in the aqueous medium at a level between about 0.05 and about 2.5 percent solids, more preferably between about 0.5 and about 1 percent.

Preferably, the aqueous medium is made up by the following procedure. Typically, the fluorochemical and stain resist compounds are provided by the manufacturer in a concentrated aqueous dispersion. These concentrates can be simply added to the remaining water in a vessel and stirred at room temperature. Because some of the fluorochemical and/or stain resist compositions are in emulsion form which can be sensitive to high shear, the stirring is preferably done at low shear. The pH is measured and the appropriate amount of acid is added to bring the pH to the desired level.

In accordance with the invention, the carpet yarn is immersed in the aqueous medium. Preferably, this is accomplished by immersing carpet in a bath of the aqueous medium. Most preferably, the carpet is immersed by drawing it through a puddle of the medium in an apparatus such as that known in the industry as a "flex nip applicator." Alternatively, the carpet can be placed in a vessel containing the aqueous medium. Still further, the aqueous medium can be sprayed or cascaded onto the carpet so as to immerse the carpet.

The amount of aqueous medium applied to the carpet is preferably such that it will provide a ratio of carpet to aqueous medium of at least about 0.5 to 1. A common expression for the amount of liquid applied to carpet is "wet pick-up." By this expression, the preferred wet pick-up is at least about 50 percent. More preferably, the wet pick-up is between about 50 percent and about 6000 percent, i.e. a ratio

of 0.5:1 to 60:1. Most preferably, the wet pick-up is between about 200 and about 500%, i.e. a ratio of 2:1 to 5:1. The control of the wet pick-up level can be accomplished by conventional means, such as squeeze rollers and the like.

Heating the aqueous dispersion in contact with the carpet yarn has been found to enhance the performance of the method of the present invention. As shown in the examples below, the heating step greatly shortens the time needed to get good exhaustion of the fluorochemical compound onto the carpet fiber. Thus, although not required, the heating step greatly improves the efficiency of the method. While not wishing to be bound by any particular theory, it is currently believed that the heat treatment helps cure or fix the molecules of fluorochemical to the carpet yarn fibers.

Preferably, this heating step is performed at between about 160° F. and 260° F. for between 15 second and about 60 minutes, more preferably between about 180° F. and about 220° F. for between about 30 seconds and about 8 minutes. Most preferably, the heating step is accomplished by exposing the carpet with the aqueous medium to steam at ambient pressure, i.e. 212° F. for about 1.5 minutes.

After the heating step, the carpet is preferably rinsed to remove excess chemicals. This rinsing can be done by conventional means.

After rinsing, the excess water is preferably removed by conventional means, such as a Bock centrifuge. Typically, the water content after centrifuging will be about 20-30 percent.

After the excess water is removed, the carpet is preferably dried in a conventional oven. Typically, the carpet is dried at about 220° F. for between about 6 and about 8 minutes.

EXAMPLES

The following examples are provided by way of explanation and illustration. As such, these examples are not to be viewed as limiting the scope of the invention as defined by the appended claims.

Ingredients and Materials

Carpet Construction

The pieces of carpet used in the following examples were made with the various face yarns as noted below:

Where the example refers to a nylon 6 staple yarn, this is a type 316 yarn from Allied Signal.

Where the example refers to a nylon 6 filament yarn, this is a type 1190 yarn from Allied Signal.

Where the example refers to a nylon 6,6 filament yarn, this is a Suessen set type 1150 yarn from DuPont.

Where the example refers to a nylon 6,6 staple yarn, this is a type 1993 staple yarn from Monsanto.

Where the example refers to a polypropylene yarn, this is a Type 1450 filament yarn from Shaw Industries, Inc.

Where the example refers to a PET filament yarn, this is a type 1450 yarn from Shaw Industries, Inc.

Where the example refers to a PET carrier staple yarn, this is a type 837 yarn from Hoechst Celanese Corp.

Where the example refers to a PET carrier staple yarn, this is a type 804 yarn from Hoechst Celanese Corp.

Where the example refers to a Superfil set yarn, this is a yarn that has been heat set with saturated steam under pressure in a continuous heat setting unit.

Where the example refers to a Suessen set yarn, this is a yarn that has been heat set with super heated steam under pressure in a continuous heat setting unit.

Each of these yarns was tufted into a polypropylene backing material by conventional methods and apparatus.

With the exception of examples 20a-20g which used full-width carpet on a production scale experiment, the carpet for the remaining examples was cut into 6"×12" sample pieces. Each of these sample pieces were weighed so that accurate chemical add-on and/or liquor wet pick-UPS could be calculated.

Fluorochemicals

FX-1367F

One of the fluorochemical compositions used in the examples below is that sold by 3M Specialty Chemicals Division under the designation "FX-1367F." This is a proprietary product with the principal ingredient being an electrochemically fluorinated type, anionic fluorochemical. FX-1367F is reported to be especially suited for application by foam to nylon, polyester, wool and acrylic carpets. The product obtained from 3M is an aqueous dispersion containing about 40-42% solids.

NRD-372

Another of the fluorochemical compositions used in the examples below is that sold by DuPont Flooring Systems under the designation "NRD-372." This is another proprietary product with the principal ingredient being a telomer fluorochemical. The product obtained from DuPont is an aqueous dispersion containing about 15-35% solids.

T232D

Yet another fluorochemical composition used in the examples below is sold by Advanced Polymers, Inc. under the designation "Texguard 232D" or "TG-232D" for short. This is likewise a proprietary product described as a fluoralkyl acrylate copolymer emulsion. Although a solids percent is not reported for this product, when dried in an oven at 220° F., the remaining solids are about 27 percent of the original weight.

Anionic Stain Resist/Binding Compounds

The following anionic stain resist/binding compounds were used in the examples below.

XP-4-49 and XP-4-50

As noted above, the second most preferred stain resist compound to use in the present invention is a polymethacrylic acid polymer referred to as XP-4-49 with small amounts of "Stainfree" from Sybron. This combination is referred to as XP-4-50.

A batch of XP-4-49 was made in a reaction vessel, equipped with a reflux condenser, heating, agitation, thermometer, and an inert gas blanket. To this vessel was added 54 lbs of methacrylic acid, 452 lbs of water, and 1.0 lbs of NaOH. This was referred to as aqueous phase A.

Monomer feed B was prepared by mixing 214 lbs of methacrylic acid, 303 lbs of water, 0.16 lbs of diallyl maleate and 2.2 lbs of NaOH.

Two catalyst feeds were also prepared. Feed C consisted of 2.2 lbs potassium persulfate and 197 lbs of water. Feed D consisted of 2.2 lbs of sodium metabisulfite and 197 lbs of water.

Mixture A was heated to a temperature of 85°-90° C. under a nitrogen blanket for 30 minutes. 1.3 lbs of potassium persulfate and 1.3 lbs of sodium metabisulfite were added to initiate the reaction, resulting in a small exotherm of 3° to 5° C. Feeds B, C and D were then added to the reaction vessel over a one hour period with the temperature of the vessel maintained at 90° to 95° C. At the end of the addition period, the batch was held at a temperature of 90° to 95° C. for one hour. During this hour, 0.35 lbs of potassium persulfate, 0.35 lbs of sodium metabisulfite and 2.2 lbs NaOH were added every 15 minutes for a total of 3 additions.

The resulting product, referred to as XP-4-49, was a slightly hazy, viscous liquid with 20.4% solids, a pH of 3.7 and a viscosity of 4800 cps measured on a Brookfield Viscometer with a #2 spindle at room temperature.

To make XP-4-50, 73.1 parts of XP-4-49, including the water in which it was made, are added to 24.5 parts water and 2.4 parts Sybron Stainfree. The solids content of the Sybron Stainfree is about 35%. Consequently, the preferred ratio of solids from the XP-4-49 polymer to the solids from the Stainfree is about 18 to 1. This mixture was a clear, 10 viscous, amber liquid with a final viscosity of 68 cps.

3M Stain Resist Compounds

Several stain resist compounds from Minnesota Mining & Mfg. Co. were tested in the examples below. FX-389 is a proprietary stain resist compound from 3M with a principal ingredient being a phenolic resin. FX-888F and FX-661 are other proprietary stain resist compounds from 3M with a polymer of methacrylic acid as the principal ingredient. Finally, FX-657 is a proprietary stain resist compound from 3M having a phenolic-methacrylic acid copolymer as the 15 principal ingredient.

Acrylic Acid and Methacrylic Acid Polymers from Rohm & Haas

The following acrylic and methacrylic acid based polymers were all obtained from Rohm & Haas: Leukotan 1027, 25 Leukotan 1028, Leukotan 970, and Leukotan 1084.

Other Stain Resist

A stain resist composition from DuPont was tested, namely SR-300. This is a proprietary product with a Styrene-maleic anhydride copolymer with a phenolic resin. Finally, a stain resist composition from Sybron Chemicals, Inc. was obtained under the designation "Janastain 100." This composition has a modified phenolic resin as the 30 principal ingredient.

Other Ingredients

The acid used to adjust the pH was commercially available urea sulfate.

Methods

Except for the variances noted below, the examples were all performed according to the following methods.

Dyeing Simulation

The pieces of carpet were first treated to simulate the dyeing process that carpet would typically encounter in the 45 total manufacturing process.

Each sample piece was identified with a laundry tag indicating the specific lab trial number. The sample pieces were placed in a horizontal lab steamer and steamed for 30 seconds, face-up, to simulate the pre-steaming step on a 50 continuous dye line.

The pre-steamed pieces were allowed to cool for 30 seconds, and then placed in a flat pan applicator, which contained the desired dyebath mixture and liquor amount. The blank dyebaths used in these examples contained a 0.105% solution weight Dowfax 2000 surfactant, and a phosphoric acid buffer to set the pH at the desired range, i.e. about 5.5. Production dyebaths contain the above two chemicals, along with desired level of dyes.

The wet-out sample pieces were then placed in a horizontal steamer for 4.0 minutes. The pieces were steamed for 2.0 minutes with the tufts facing up, and the final 2.0 minutes with the tufts facing down, to give good liquor flow.

The steamed pieces were then removed from the steamer and immersed in a 3 gallon volume of ambient tap water, for 10 to 15 seconds, to simulate a washing step. The pieces were then extracted in a high speed BOCK centrifuge for 4.0

minutes to pull the moisture level down to the 20-30% wet pick-up range.

Application of Stain Resist Compound and/or Fluorochemical

Application of Fluorochemical from a Bath

In some of the examples below, a fluorochemical was applied by immersing the extracted sample pieces in an aqueous dispersion containing one of the fluorochemical compositions described above. The liquor in the flat pan applicator for these examples was made up with anionic fluorochemical in the range of 0.010% to 0.090% solids, and an acid for pH adjustment to the desired range. The extracted fabric was wet out in this liquor, in the 350-400% wet-pick-up range, and subsequently steamed.

Simultaneous Application of Fluorochemical and Stain Resist Compound

In some other of the examples below, a fluorochemical and an anionic polymer stain resist compound were applied simultaneously. This was accomplished by immersing the extracted sample pieces in an aqueous dispersion containing both a fluorochemical and an anionic polymer stain resist compound. The liquor in the flat pan applicator for these examples was made up with anionic polymers in the solids range of 0.100 to 0.290% solids, anionic fluorochemical in the range of 0.010% to 0.090% solids, and an acid for pH adjustment into the range of 1.5-1.80. The extracted fabric was wet out in this liquor, in the 350-400% wet-pick-up range, and subsequently steamed.

Conventional Stain Resist Compound Application

In still other of the examples below, a conventional application of an anionic polymer stain resist compound was used. This was accomplished by immersing the sample piece in a solution of the stain resist compound to be used. Specifically, after the centrifuge extraction step described above, the sample pieces were again placed in a flat pan applicator that contains a conventional stain resist compound liquor. The application wet-pick-up was 400%. The typical conventional stain resist compound bath contained a stain resist compound at 0.120 to 0.290% solids, and an acid (typically Urea Sulfate) to adjust the pH to the desired range. The typical pH range for conventional stain resist compound application was 2.0-2.5.

Conventional Fluorochemical Application

In still other examples performed for purposes of comparison, a fluorochemical was applied in a way to simulate a conventional application, as a topical treatment by a spray bar in a step subsequent to the application of a stain resist compound. In these example, the extracted sample pieces, were placed in a flat pan, pile down, for application of a solution containing fluorocarbon in the range of 0.15 to 1.75% solids, with the pH in the range of 3.5-7.5 units. The lab application is made in the 100% wet-pick-up range to ensure adequate pile penetration for the solution. The pieces with this conventional application of fluorochemical were dried without the steam fixation or rinse extraction step described below.

Steaming

The wet-out sample pieces were placed in the horizontal steamer for 1.5 minutes of steaming to fix the fluorochemical, the stain resist compound or the combination of both on the carpet fibers. The fabric was steamed for 45 seconds with the tufted pile up, and 45 seconds with the tufted pile down to achieve liquor flow.

Rinse/Extraction

The steamed sample pieces were then removed from the steamer and immersed in a 3 gallon volume of ambient tap water, for 10 to 15 seconds, to simulate a washing step. The

sample pieces were then extracted in a high speed BOCK centrifuge for 4.0 minutes to pull the moisture level down to the 20-30% WPU range.

Drying

The extracted sample pieces, or the pieces with a topical application of fluorochemical, were then placed, with the pile up, in an electrically heated, forced air oven operating at 220° F. for 6-8 minutes. The sample pieces had a moisture content in the range of 1-2% when removed from the oven.

Test Methods

The products of the examples were tested by one or more of the following test methods:

PPM Fluorine

The test to measure the level of fluorochemical applied to the carpet samples below was the "NYLON FLUORINE CONTENT—COMBUSTION FLASK OXIDATION/SPECIFIC ION METER" test published in October 1983 by the Textile Fibers Department of E. I. DuPont De Nemours & Company, Inc. under the number TM-371-66, N-M 27414.00. Briefly stated, the test is conducted by burning the sample in an oxygen combustion flask. The fluoride is absorbed in a sodium hydroxide solution and the pH and ionic strength of that solution is adjusted. The concentration (activity) of the fluoride ion is measured potentiometrically. The results are reported as parts per million fluorine.

Repellency Tests

The following tests were run to determine the repellency of the carpet samples:

Oil Repellency

The test method published in December 1992 by 3M Specialty Chemicals Division as "3M Carpet Oil Repellency Test III" was used below. In this test, five 5 mm drops of oil are placed from a height of 3 mm onto the carpet surface to be tested. The oil used is supplied by 3M under the designation "Oily Test Liquid C." If after 10 seconds, four out of the five drops are still visible as spherical to hemispherical, the carpet is given a passing rating. Some samples are given a "marginal" rating, designated by a "(M)" after the P or F, and meaning that the sample narrowly passed, or narrowly failed.

Water Repellency

The test method published in December 1992 by 3M Specialty Chemicals Division as "3M Carpet Water Repellency Test V" was also used below. This test is the same as the oil repellency test above, with the exception that drops of deionized water are used in place of oil.

Water/Alcohol Repellency

The samples were also tested to determine the repellency to a water and alcohol mixture. Specifically, the same procedure as the water repellency test above was used except that, instead of water, a mixture of 90% deionized water and 10% isopropyl alcohol was used.

Soil Repellency

The samples from examples 20a-q were also tested for repellency to soiling. This was accomplished through the use of a device sold by James H. Heal & Co. of Yorkshire England under the designation "Kappasol Rapid Soil Applicator." The object of this device is to replicate traffic and soiling conditions on carpet. This is done by placing carpet samples to fit on the turntable on the device. The turntable rotates the sample through a set number of revolutions and

reverses the direction at a set interval so that the pile is uniformly "trafficked" from each direction.

As the turntable rotates, a synthetic soil is metered into the device and applied to the carpet. Face rollers on the turntable mechanically force the soil into intimate contact with the carpet pile. After the predetermined number of revolutions, the carpet samples are removed from the device and lightly vacuumed to pull off loosely adhered soil.

The samples are then graded for color change versus an unsold control. While this can be done manually, with the AATCC grey scale, it was done for examples 20a-q by the use of a MacBeth Eagle-Eye spectrophotometer. The reflectance data was converted to L*a*b* units using the 1976 CIE L*a*b* color equations. The data reported below is the ΔL* values which indicate the degree of darkening, due to soiling, of the samples soiled in the Kappasol tester as compared to the unsold control. Low absolute values of ΔL* indicate a low degree of darkening due to soil adhering to the carpet fibers, thus a low degree of soiling potential relative to samples with higher ΔL* values.

Stain Resistance

Resistance to Staining by Acid Red #40

The test method published in December 1992 by 3M Specialty Chemicals Division as "3M Carpet Stain Release Test II" was used below. In this test, the stain resistance of a carpet sample is tested by applying a small volume of an aqueous solution of Food, Drug & Cosmetic Red 40. The staining solution is made with 80 mg. of dye per liter of deionized water and has a pH of 3.0±0.2. A staining ring with a 2 inch opening is used to apply 20 ml of the staining solution on the carpet sample. Once the 20 ml is absorbed into the carpet, the staining ring is removed and the sample is left undisturbed for 24±2 hrs. The sample is rinsed with tap water until the rinse water is clear. Excess water is removed and the sample is oven dried at about 100° C for 90 minutes. The sample is then rated against the grey scale for color change provided by the American Association of Textile Colorist and Chemists (AATCC). This scale goes from 1 to 5 with 1 indicating severe color change and 5 indicating no color change. A score of 4 is generally considered acceptable on this test.

Resistance to Staining by Mustard

The resistance to staining by mustard is conducted in a manner similar to that for Acid Red #40, with the exception that the staining solution is made by adding 75 grams of French's mustard (containing turmeric) to 1 liter of tap water. The carpet samples are allowed to sit in the mustard mixture for 30 seconds then drained. After sitting for 24 hrs., the samples are rinsed and dried. After drying the samples are rated on the same AATCC grey scale for color change.

Resistance to Staining by Coffee at 140° F.

The test for resistance to staining by coffee is similar to that for mustard. The staining solution is made from regular strength instant coffee brewed and brought to a temperature of about 140° F. The carpet samples were immersed in the coffee for 30 seconds. The samples were allowed to sit for 30 minutes, then rinsed and dried. After drying, the samples were rated on the same AATCC grey scale for color change. A score of 4 is generally considered acceptable on this test. "WAQE" Stain Resistance Durability Test

The samples in examples 20a-k were tested to determine the durability of the stain resistant properties. This is accomplished by mixing up a detergent solution containing 2.2 oz. of DuPont's "DuPont/WAQE" detergent per gallon of water. The pH of this solution is adjusted to 10.0 with a 10

percent TriSodium Phosphate solution. Samples of the carpet to be tested are then immersed in the detergent solution for 5 minutes. The sample is then rinsed thoroughly under a faucet, hand squeezed and extracted with a centrifugal extractor to remove excess water. After the carpet has been thus treated and dried, the same stain resistance test with Acid Red No. 40 is performed and the color difference is rated by the same AATCC grey scale.

Other Tests for Colorfastness

Exposure to Ozone

Some of the samples in examples 20a-q were also tested for colorfastness when exposed to ozone. In particular, the AATCC test method 129-1990 was performed and the exposed samples were graded on the AATCC grey scale.

Exposure to NO_x

Some of the samples in examples 20a-q were also tested for colorfastness when exposed to NO_x. In particular, the AATCC test method 164-1987 was performed and the exposed samples were graded on the AATCC grey scale.

Exposure to Xenon Lamp

The samples in examples 20a-q were also tested for colorfastness when exposed to light from a xenon lamp for 40 hours. In particular, the AATCC test method 16-1990 was performed and the exposed samples were graded on the AATCC grey scale.

Fluorochemical Penetration

The carpet from examples 20a-q were also tested to determine the penetration of the fluorochemical treatment. This was accomplished by first measuring the average pile height of a 1 by 3 inch sample of carpet. Then, a quantity of Wesson oil with 0.2 g of oil red 0 per gallon of oil was placed in a clear baking dish. The carpet sample was placed in the dish so that the oil came just over the top of the primary backing. The samples were left in the dish for 45 minutes. The average height of oil absorbed on the yarn from the carpet backing for each pile height was then measured. The results are reported as the percentage of the average pile height which did not have oil absorbed on it over the entire average pile height. Thus, the higher the percentage, the further down the fluorochemical penetrated into the pile.

EXAMPLES 1a-1p

Application of Fluorochemicals Alone and With Stain resist compounds on Nylon

Examples 1a-1p were performed to demonstrate the invention on nylon 6 and nylon 6,6 of carpet face fiber. The yarn in examples 1a-1h was the nylon 6 yarn described above. In examples 1a-1d, the yarn was Suessen set and tufted at 32 osy. In examples 1e-1h, the yarn was Superba set and was tufted at 25.5 osy. The yarn in examples 1i-1p was the nylon 6,6 yarn described above. In examples 1i-1l, the yarn was Suessen set and was tufted at 30.3 osy. In examples 1m-1p, the yarn was Superba set and was tufted at 35 osy.

All of the 16 carpet sample pieces were prepared as described above, i.e. including the dye bath simulation. As noted in Table 1 below, the extracted pieces were then treated with either the FX1367F or the T232D fluorochemical alone or one of those fluorochemicals together with the XP-4-50 stain resist compound by the methods described above. In all of examples 1a-1p, the pH of the bath was 1.8

and the wet pick-up was 400%. The pieces were steamed, washed, extracted and dried all as described above.

After drying, the sample carpet pieces were each tested for oil, water, and water/alcohol repellency and for fluorine content by the test methods described above. The results are reported in Table 1.

As can be seen the FX1367 (compare examples 1a to 1b, 1i to 1j, and 1m to 1n) was more impacted by the addition of the XP-4-50 to the application bath than was the T232D (compare examples 1c to 1d, 1k to 1l, and 1o to 1p).

TABLE 1

No.	Fiber Type	FX 1367	T232D	XP-4-50	Oil	H ₂ O	H ₂ O/Ac	ppm F
1a	N6 Suessen	X			P	P	P	367
1b		X		X	P	P	P	128
1c			X		P	P	P	416
1d			X	X	P	P	P	320
1e	N6 Superba	X			P	P	P	553
1f		X		X	P	P	P	321
1g			X		P	P	P	389
1h			X	X	P	P	P	309
1i	N6,6 Suessen	X			P	P	P	267
1j		X		X	P	P	P	104
1k			X		P	P	P	384
1l			X	X	P	P	P	272
1m	N6,6 Superba	X			P	P	P	473
1n		X		X	P	P	P	126
1o			X		P	P	P	397
1p		X	X	X	P	P	P	289

EXAMPLES 2a-2p

Application of Fluorochemical Alone and With Stain Resist compound on PET and PP

Examples 2a-2p were performed exactly as examples 1a-1p except that different types of face fibers were used. In examples 2a-2d, the yarn was as the Superba set PET filament described above and was tufted at 33 osy. In examples 2e-h, the yarn was the carrier polyester staple described above and was tufted at 34 osy. In examples 2i-2l, the yarn was the carrier polyester staple from Hoechst Celanese described above and was tufted at 40 osy. In examples 2m-2p, the yarn was the Superba set polypropylene filament produced by Shaw Industries, Inc. described above tufted at 26 osy. The results are reported in Table 2.

These results show that the T232D worked better on the PET samples than did the FX 1367. Also, as can be seen by comparing examples 2m to 2n and 2o to 2p, the addition of the anionic binding polymer XP-4-50 greatly enhanced the performance of both fluorochemicals on the polypropylene samples.

TABLE 2

No.	Fiber Type	FX 1367	T232D	XP-4-50	Oil	H ₂ O	H ₂ O/Ac	ppm F
2a	PET Superba	X			P	P	P	124
2b		X		X	P	P	P	111
2c			X		P	P	P	304
2d			X	X	P	P	P	224
2e	PET 837	X			P	P	P	166
2f			X		P	P	P	861
2g				X	P	P	P	346

TABLE 2-continued

No.	Fiber Type	FX 1367	T232D	XP-4-50	Oil	H ₂ O	H ₂ O/Ac	ppm F
2h		X	X	P	P	P	253	
2i	PET 804	X		P	P	P	126	
2j		X	X	P	P	P	76	
2k		X	X	P	P	P	212	
2l		X	X	P	P	P	216	
2m	PP Superba	X		F	P	P	135	10
2n		X	X	P	P	P	229	
2o			X	F	P	P	90	
2p		X	X	P	P	P	313	

EXAMPLES 3a-3i

Application of Fluorochemical with XP-4-50 and SR-300 on Polypropylene

Examples 3a-3h were performed exactly as examples 2m-2p except that the Superba set polypropylene yarn was tufted at 22 osy, two different pH levels for the bath were used and the XP-4-50 and SR-300 stain resist compounds were compared. Example 3i was tested as a control. Example 3i was made with the 22 osy Superba set polypropylene yarn, was treated in the dye bath simulation, but was not treated to add either fluorochemical or stain resist compound. The results are reported in Table 3.

These results indicate that the XP-4-50 did generally better than the SR-300 when applied to polypropylene.

the level of fluorine as described above. The results are reported in Table 4.

These results show the dramatic decline in fluorochemical performance when the pH of the application bath is not below about 3.5.

TABLE 4

Ex. No.	pH	Oil	Water	Water/ Alcohol	ppm F
4a	1.5	P	P	P	757
4b	1.6	P	P	P	787
4c	1.7	P	P	P	769
4d	1.8	P	P	P	749
4e	1.9	P	P	P	698
4f	2.0	P	P	P	731
4g	2.1	P	P	P	733
4h	2.2	P	P	P	737
4i	2.5	P	P	P	388
4j	3.0	P	P	P	372
4k	3.5	P	P	P	50
4l	4.0	P(M)	F	F	32
4m	4.5	F	F(M)	F(M)	42
4n	5.0	F	F	F	30
4o	5.5	F	F	F	34
4p	6.0	F	F	F	61

EXAMPLES 5a-5p

pH Effect on Fluorochemical Only Applied to Nylon 6

Examples 5a-5p were performed and tested exactly the same as Examples 4a-4p with the exception that the nylon

TABLE 3

No.	pH	FX 1367	T232D	XP-4-50	SR-300	Oil	H ₂ O	H ₂ O/Ac	ppm F
3a	1.8	X		X		P	P	P	184
3b	1.5	X		X		P	F	283	
3c	1.8		X	X		P	P	P	391
3d	1.5		X	X		P	P	P	317
3e	1.8	X			X	F(M)	P	P	143
3f	1.5	X			X	P	P	P	188
3g	1.8	X			X	P	P	P	163
3h	1.5	X			X	P	P	P	237
3i	1.8					F	P	N/A	

EXAMPLES 4a-4p

pH Effect on Fluorochemical Only Applied to Nylon 6,6

Examples 4a-4p were performed to observe the effect of the pH of the aqueous dispersion of fluorochemical. The carpet sample pieces used in these examples were made with the nylon 6,6 yarn described above which was Superba set also as described above. The yarn was tufted to give a density of 35 osy. The carpet sample pieces were all treated in the dye bath simulation method described above. A fluorochemical was then applied by the immersion method described above. The liquor for the fluorochemical application included 0.6% of the NRD372 composition described above and urea sulfate to adjust the pH to the level noted below. The balance of the liquor was water. The pieces were steamed, rinsed, extracted and dried as described above. The carpet sample pieces were then tested in the oil repellency, water repellency, and water/alcohol repellency tests described above. The pieces were also tested to determine

6 yarn described above was used in place of the nylon 6,6 yarn. The nylon 6 yarn was Superba set and was tufted at 25.5 osy. The results are in Table 5.

These results show the decline in fluorochemical performance on nylon 6 when the pH is 3 or above.

TABLE 5

Ex. No.	pH	Oil	Water	Water/ Alcohol	ppm F
5a	1.5	P	P	P	750
5b	1.6	P	P	P	768
5c	1.7	P	P	P	759
5d	1.8	P	P	P	683
5e	1.9	P	P	P	698
5f	2.0	P	P	P	640
5g	2.1	P	P	P	675
5h	2.2	P	P	P	633
5i	2.5	P	P	P	389
5j	3.0	F	F	F	61
5k	3.5	F	F	F	43
5l	4.0	F	F	F	29
5m	4.5	F	F	F	34

TABLE 5-continued

Ex. No.	pH	Oil	Water	Water/ Alcohol	ppm F
5a	5.0	F	F	F	36
5b	5.5	F	F	F	41
5c	6.0	F	F	F	38

5

EXAMPLES 6a-6h

pH Effect on Fluorochemical and Anionic Polymer Applied to Nylon 6,6

Examples 6a-6h were performed and tested exactly the same as Examples 4a-4h with the exception that the XP-4-50 anionic polymer stain resist compound described above was added to the liquor with the NRD372 fluorochemical. The XP-4-50 solution was added at 3.3% giving a weight solids level of 0.120%. The results of the tests are in shown Table 6.

These results demonstrate preferred maximum pH of 1.8 when the fluorochemical and stain resist compound are applied simultaneously to nylon 6,6.

10

TABLE 6

Ex. No.	pH	Oil	Water	Water/ Alcohol	ppm F
6a	1.5	P	P	P	582
6b	1.6	P	P	P	582
6c	1.7	P	P	P	545
6d	1.8	P	P	P	316
6e	1.9	P	P	F	87
6f	2.0	P	F	F	62
6g	2.1	P	F	F	42
6h	2.2	P	F	F	41

25

EXAMPLES 7a-7h

pH Effect on Fluorochemical and Anionic Polymer Applied to Nylon 6

Examples 7a-7h were performed and tested exactly the same as Examples 5a-5h with the exception that the XP-4-50 anionic polymer stain resist compound described above was added to the liquor with the NRD372 fluorochemical. The XP-4-50 solution was added at 3.3% giving a weight solids level of 0.120%. The results of the tests are in shown Table 7.

Though not as dramatic, these results show the preferred maximum pH of 2.0 when working with nylon 6.

40

TABLE 7

Ex. No.	pH	Oil	Water	Water/ Alcohol	ppm F
7a	1.5	P	P	P	522
7b	1.6	P	P	P	457
7c	1.7	P	P	P	489
7d	1.8	P	P	P	602
7e	1.9	P	P	P	452
7f	2.0	P	P	P	319
7g	2.1	F	P	P	195
7h	2.2	F	P	P	208

60

EXAMPLES 8a-8i

Effect of Time on Fluorochemical and Anionic Polymer Applied to Nylon 6,6 Without a Heating Step at pH of 1.5

Examples 8a-8i were performed to study the effect of time on samples having a fluorochemical and stain resist compound applied without a heating step. With the exception of the time the carpet samples were left in contact with the aqueous medium and the absence of a heating step, examples 8a-8h were performed the same as example 6a, i.e. with a pH of the aqueous medium being set at 1.5. Example 8i was performed as a control and included a 3 minute steam treatment. The results of the tests on these samples, including the Acid Red 40 stain test, are in shown Table 8.

These results show that the performance of the fluorochemical application without a heating step improves with dwell time.

TABLE 8

Ex. No.	time (hrs.)	AR 40	Oil	Water	Water/ Alcohol	ppm F
8a	1	2	F	P	P	116
8b	2	2-3	P	P	P	135
8c	3	3	P	P	P	165
8d	4	3-4	P	P	P	206
8e	8	3-4	P	P	P	264
8f	24	4	P	P	P	273
8g	48	4	P	P	P	258
8h	72	4-5	P	P	P	257
8i	3 min.	5	P	P	P	297

EXAMPLES 9a-9f

Effect of Time on Fluorochemical and Anionic Polymer Applied to Nylon 6,6 Without a Heating Step at pH of 1.8

Examples 9a-9f were performed the same as examples 8d-8i, with the one exception that the aqueous medium was prepared with a pH of 1.8. Example 9f was performed as a control and included a 3 minute steam treatment. The results of the tests on these samples, including the Acid Red 40 stain test, are in shown Table 9.

Comparing these results with those from Table 8 shows that the pH of 1.5 in examples 8a-h gave better results than the pH of 1.8 in examples 9a-e.

TABLE 9

Ex. No.	time (hrs.)	AR 40	Oil	Water	Water/ Alcohol	ppm F
9a	4	2	F	P	FOM)	73
9b	8	3-4	F	P	FOM)	89
9c	24	3	F	P	F	80
9d	48	4	F	P	FOM)	93
9e	72	4	F	P	P	88
9f	3 min.	4	P	P	P	346

EXAMPLES 10a-10i

Effect of Time on Fluorochemical and Anionic Polymer Applied to Nylon 6 Without a Heating Step at pH of 1.5

Examples 10a-10i were performed exactly the same as examples 8a-8i with the exception that the Superba set nylon 6 yarn described above tufted at 25.5 oys was used

instead of the nylon 6,6. The results of the tests on these samples are in shown Table 10.

These results are similar to those with nylon 6,6 in examples 8a-i.

TABLE 10

Ex. No.	time (hrs.)	AR 40	Oil	Water	Water/ Alcohol	ppm F
10a	1	1-2	F	P	P	95
10b	2	2	F	P	P	123
10c	3	2	P	P	P	157
10d	4	2-3	P	P	P	233
10e	8	2-3	P	P	P	251
10f	24	2-3	P	P	P	249
10g	48	2-3	P	P	P	283
10h	72	3	P	P	P	285
10i	3 min.	2	P	P	P	270

EXAMPLES 11a-11f

Effect of Time on Fluorochemical and Anionic Polymer Applied to Nylon 6 Without a Heating Step at pH of 1.8

Examples 11a-11f were performed the same as examples 9a-9f, with the one exception that the Superba set nylon 6 yarn described above tufted at 25.5 osy was used instead of the nylon 6,6. The results of the tests on these samples are

TABLE 11-continued

Ex. No.	time (hrs.)	AR 40	Oil	Water	Water/ Alcohol	ppm F
11e	72	3	F	P	P	91
11f	3 min.	2	P	P	P	301

10

EXAMPLES 12a-12x

Various Anionic Polymers Applied to Nylon 6 at 1.0% solids and a pH of 1.5

15

Examples 12a-12k were performed to compare the use of various anionic binder polymers used with two different fluorochemical compounds. In particular, 12 different anionic polymers, all described above, were applied in a bath which contained either the T232D fluorochemical or the FX1367F fluorochemical. The carpet was made from nylon 6 tufted at 25.5 osy. In each example, the anionic polymer was present at about 0.25% of the bath. When used, the T232D fluorochemical was present at about 0.0135 % of the bath. When used, the FX1367F fluorochemical was present at 0.05% of the bath. The pH of the bath was adjusted to 1.5. The other levels, as well as the methods, times and temperatures were the same as in examples 1. The results of the tests on these samples are in shown Table 12.

20

25

TABLE 12

Ex. No.	Anionic Polymer	FC Used	AR 40	Oil	Water	Water/ Alcohol	ppm F
12a	FX369	T232D	5	F	F(M)	F	63
12b	FX369	FX1367F	5	F	F(M)	F	102
12c	FX668	T232D	5	F	P	P	87
12d	FX668	FX1367F	5	P	F(M)	F	76
12e	FX661	T232D	5	F(M)	P	P	61
12f	FX661	FX1367F	5	F(M)	F(M)	F	78
12g	FX561	T232D	5	P	P	P	170
12h	FX561	FX1367F	4-5	P	P	P	208
12i	SR300	T232D	2-3	P	P	P	136
12j	SR300	FX1367F	2-3	P	P	P	200
12k	LK1027	T232D	5	F	P	P	82
12l	LK1027	FX1367F	5	F(M)	P	P	170
12m	LK1028	T232D	4-5	F	P	F(M)	148
12n	LK1028	FX1367F	4-5	F	F(M)	F	159
12o	LK970	T232D	4-5	F	P	F	148
12p	LK970	FX1367F	4-5	F(M)	F(M)	F	180
12q	LK1084	T232D	1-2	F	F	F	55
12r	LK1084	FX1367F	1-2	P	P	F	135
12s	TS100	FX1367F	4	F	F	F	51
12t	TS100	FX1367F	4-5	F	F	F	49
12u	XP-4-49	T232D	4-5	F(M)	P	P	120
12v	XP-4-49	FX1367F	4-5	F(M)	P	F	203
12w	XP-4-50	T232D	5	F	P	P	167
12x	XP-4-50	FX1367F	5	P	P	F(M)	185

55

EXAMPLES 13a-13x

in shown Table 11.

These results are similar to those for nylon 6,6 in Table 9.

TABLE 11

60

Ex. No.	time (hrs.)	AR 40	Oil	Water	Water/ Alcohol	ppm F
11a	4	2-3	F	P	F(M)	73
11b	8	2	F	P	F(M)	68
11c	24	2-3	F	P	F	74
11d	48	2-3	F	P	F	71

Various Anionic Polymers Applied to Nylon 6 at 0.5% solids and a pH of 1.5

Examples 13a-13x were performed the same as examples 12a-12x with the sole exception that half the amount of anionic polymer was added to the liquor so that it was applied at 0.5% by weight solids. The results of the tests are shown in Table 13. Comparing the results in Table 12 with the results in Table 13 shows that the reduced level of

anionic binding polymer in examples 13a-13x produces better fluorochemical performance.

TABLE 13

Ex. No.	Anionic Polymer	FC Used	AR 40	Oil	Water	Water/ Alcohol	ppm F
13a	FX369	T232D	3	P	P	P	161
13b	FX369	FX1367F	2	P	P	P	202
13c	FX668	T232D	4	P	P	P	110
13d	FX668	FX1367F	3-4	P	P	P	108
13e	FX561	T232D	2	P	P	P	117
13f	FX661	FX1367F	3-4	P	P	P	88
13g	FX567	T232D	1-2	P	P	P	160
13h	FX567	FX1367F	1-2	P	P	P	175
13i	SR300	T232D	1	P	P	P	164
13j	SR300	FX1367F	1	P	P	P	212
13k	LK1027	T232D	2-3	FOM	P	P	126
13l	LK1027	FX1367F	1-2	P	FOM	FOM	183
13m	LK1028	T232D	4-5	F	P	FOM	152
13n	LK1028	FX1367F	4-5	FOM	FOM	FOM	162
13o	LK970	T232D	2	FOM	P	FOM	156
13p	LK970	FX1367F	1	P	FOM	FOM	197
13q	LK1084	T232D	1	F	P	FOM	76
13r	LK1084	FX1367F	1	P(M)	F	F	172
13s	TS100	T232D	3-4	F	FOM	F	42
13t	TS100	FX1367F	4	F	FOM	F	60
13u	XP-4-49	T232D	3-4	F	FOM	F	104
13v	XP-4-49	FX1367F	4	F	FOM	F	201
13w	XP-4-50	T232D	4-5	F	P	FOM	99
13x	XP-4-50	FX1367F	4-5	P	P	FOM	238

EXAMPLES 14a-14x

30

Various Anionic Polymers Applied to Nylon 6 at 1.0% solids and a pH of 1.8

Examples 14a-14x were performed the same as examples 12a-12x with the sole exception that the pH of the bath was ³⁵ adjusted to 1.8. The results of the tests are shown in Table 14.

EXAMPLES 15a-15x

Various Anionic Polymers Applied to Nylon 6 at 0.5% solids and a pH of 1.8

Examples 15a-15x were performed the same as examples 14a-14x with the sole exception that half the amount of anionic polymer was added to the liquor so that it was applied at 0.5% by weight solids. The results of the tests are

TABLE 14

Ex. No.	Anionic Polymer	FC Used	AR 40	Oil	Water	Water/ Alcohol	ppm F
14a	FX369	T232D	5	F	F	F	39
14b	FX369	FX1367F	5	F	F	F	75
14c	FX668	T232D	5	F	P	FOM	53
14d	FX668	FX1367F	5	F	F	F	58
14e	FX561	T232D	5	F	P	F	39
14f	FX561	FX1367F	5	P	FOM	F	40
14g	FX567	T232D	5	P	P	P	168
14h	FX567	FX1367F	5	P(M)	FOM	FOM	130
14i	SR300	T232D	2-3	P	P	P	132
14j	SR300	FX1367F	4	P	P	FOM	104
14k	LK1027	T232D	5	F	P	P	82
14l	LK1027	FX1367F	5	P	POM	POM	170
14m	LK1028	T232D	4-5	F	P	P	145
14n	LK1028	FX1367F	4-5	FOM	POM	FOM	194
14o	LK970	T232D	3	F	P	FOM	136
14p	LK970	FX1367F	3	FOM	FOM	F	240
14q	LK1084	T232D	1-2	F	F	F	62
14r	LK1084	FX1367F	1-2	P	F	F	131
14s	TS100	T232D	3-4	F	F	F	39
14t	TS100	FX1367F	4-5	F	F	F	37
14u	XP-4-49	T232D	4-5	F	P	FOM	127
14v	XP-4-49	FX1367F	4-5	P	P	FOM	185
14w	XP-4-50	T232D	5	F	P	P	129
14x	XP-4-50	FX1367F	5	P	P	FOM	177

⁶⁵ shown in Table 15. Similar to the comparison of Tables 12 and 13, comparison of tables 14 and 15 show that the performance of the fluorochemical was improved with the

reduced level of anionic binding polymer in examples 15a-x.

TABLE 15

Ex. No.	Anionic Polymer	FC Used	AR 40	Oil	Water	Water/ Alcohol	ppm F
15a	FX369	T232D	3-4	F	P	F(M)	53
15b	FX369	FX1367F	2-3	F	F(M)	F	75
15c	FX368	T232D	3	P	F(M)	P	110
15d	FX368	FX1367F	3	F(M)	P	P	108
15e	FX361	T232D	2-3	P	P	P	117
15f	FX361	FX1367F	4-5	P	F(M)	F(M)	88
15g	FX367	T232D	3	P	P	P	160
15h	FX367	FX1367F	2	P	P	F(M)	175
15i	SR300	T232D	1	P	P	P	164
15j	SR300	FX1367F	1	P	P	P	212
15k	LK1027	T232D	2	P(M)	P	P	126
15l	LK1027	FX1367F	2	P	F(M)	F(M)	183
15m	LK1028	T232D	4-5	F(M)	P	F(M)	152
15n	LK1028	FX1367F	4-5	P(M)	F(M)	P	162
15o	LK970	T232D	1	P	P	P	156
15p	LK970	FX1367F	1	P	P	P(M)	197
15q	LK1084	T232D	1	P	P	P(M)	76
15r	LK1084	FX1367F	1	P(M)	F(M)	F	172
15s	TS100	T232D	3	F	F	F	42
15t	TS100	FX1367F	3-4	F	F	F	60
15u	XP-4-49	T232D	3-4	F	P	F	104
15v	XP-4-49	FX1367F	4	F	F(M)	F	201
15w	XP-4-50	T232D	5	P	P	F(M)	188
15x	XP-4-50	FX1367F	4-5	P	P	F(M)	93

EXAMPLES 16a-16x

30

Various Anionic Polymers Applied to Nylon 6,6 at 1.0% solids and a pH of 1.5

Examples 16a-16x were performed the same as examples 12a-12x with the sole exception that the carpet used was made from nylon 6,6 Superba set yarn tufted at 35 osy. The results of the tests are shown in Table 16. The results for these examples with nylon 6,6 are similar to those found in Table 12 for nylon 6.

EXAMPLES 17a-17x

Various Anionic Polymers Applied to Nylon 6,6 at 0.5% solids and a pH of 1.5

Examples 17a-17x were performed the same as examples 16a-16x with the sole exception that half the amount of anionic polymer was added to the liquor so that it was applied at 0.5% by weight solids. The results of the tests are shown in Table 17.

TABLE 16

Ex. No.	Anionic Polymer	FC Used	AR 40	Oil	Water	Water/ Alc.	ppm F
16a	FX369	T232D	5	F	F	F	37
16b	FX369	FX1367F	5	P	F(M)	F	70
16c	FX368	T232D	5	F	F(M)	F	52
16d	FX368	FX1367F	5	F	F(M)	F	44
16e	FX361	T232D	5	F	P	F	45
16f	FX361	FX1367F	5	F	P(M)	F	57
16g	FX657	T232D	5	P	P	P	154
16h	FX657	FX1367F	5	P	P	P	215
16i	SR300	T232D	5	P	P	P	135
16j	SR300	FX1367F	5	P	P	P	180
16k	LK1027	T232D	5	F	P	P	85
16l	LK1027	FX1367F	5	F(M)	P	F	187
16m	LK1028	T232D	4-5	F	P	F(M)	142
16n	LK1028	FX1367F	4-5	F	F(M)	F(M)	192
16o	LK970	T232D	4-5	F	F(M)	F	136
16p	LK970	FX1367F	4-5	F	F(M)	F	161
16q	LK1084	T232D	1-2	F(M)	F	F	72
16r	LK1084	FX1367F	1-2	P(M)	F	F	170
16s	TS100	T232D	4-5	F	F	F	51
16t	TS100	FX1367F	5	F	F	F	40
16u	XP-4-49	T232D	4-5	F(M)	P(M)	F(M)	128
16v	XP-4-49	FX1367F	4-5	F(M)	P	F(M)	166
16w	XP-4-50	T232D	5	F(M)	P	P	125
16x	XP-4-50	FX1367F	5	P	P	P	230

Though not as dramatic as the comparison between Tables 12 and 13, the comparison of the results in Tables 16 and 17 shows that the performance of the fluorochemical is enhanced with the lower level of anionic binding polymer.

TABLE 17

Ex. No.	Anionic Polymer	FC Used	AR 40	Oil	Water	Water/ Alcohol	ppm F
17a	FX369	T232D	5	F	P(M)	F	44
17b	FX369	FX1367F	5	F	P(M)	F	59
17c	FX668	T232D	5	F	P	P(M)	61
17d	FX668	FX1367F	5	F	P(M)	P(M)	97
17e	FX661	T232D	5	F	P	P(M)	68
17f	FX661	FX1367F	5	F	P(M)	F	80
17g	FX657	T232D	5	P	P	P	142
17h	FX657	FX1367F	5	P	P	P(M)	217
17i	SR300	T232D	3-4	P	P	P	151
17j	SR300	FX1367F	4-5	P	P	P	129
17k	LK1027	T232D	5	P(M)	P	P(M)	149
17l	LK1027	FX1367F	5	P	P	P(M)	224
17m	LK1028	T232D	4-5	P(M)	P	P(M)	140
17n	LK1028	FX1367F	4-5	P(M)	P	P(M)	189
17o	LK970	T232D	4-5	P(M)	P	F	133
17p	LK970	FX1367F	4-5	P(M)	P(M)	F	184
17q	LK1084	T232D	1	P(M)	F	F	109
17r	LK1084	FX1367F	1	P(M)	F	F	145
17s	TS100	T232D	4-5	F	P(M)	F	49
17t	TS100	FX1367F	4-5	F	P	F	60
17u	XP-4-49	T232D	4-5	F	P	P	79
17v	XP-4-49	FX1367F	4-5	F	P	P(M)	150
17w	XP-4-50	T232D	5	P(M)	P	P	104
17x	XP-4-50	FX1367F	5	P	P	P	247

EXAMPLES 18a-18x

Various Anionic Polymers Applied to Nylon 6,6 at 1.0% solids and a pH of 1.8

35

Examples 18a-18x were performed the same as examples 16a-16x with the sole exception that the pH of the bath was adjusted to 1.8. The results of the tests are shown in Table 18.

TABLE 18

Ex. No.	Anionic Polymer	FC Used	AR 40	Oil	Water	Water/ Alcohol	ppm F
18a	FX369	T232D	5	F	F	F	50
18b	FX369	FX1367F	5	F	P(M)	F	59
18c	FX668	T232D	5	F	P(M)	F	70
18d	FX668	FX1367F	5	F	P(M)	F	56
18e	FX661	T232D	5	F	P(M)	F	32
18f	FX661	FX1367F	5	F	P(M)	F	34
18g	FX657	T232D	5	P	P	P	135
18h	FX657	FX1367F	5	P(M)	P(M)	P(M)	108
18i	SR300	T232D	5	P	P	P	147
18j	SR300	FX1367F	5	P(M)	P	P(M)	108
18k	LK1027	T232D	5	F	P	P	86
18l	LK1027	FX1367F	5	P(M)	P	P	178
18m	LK1028	T232D	4-5	F	P	P(M)	145
18n	LK1028	FX1367F	4-5	F	P(M)	P(M)	168
18o	LK970	T232D	4-5	F	P(M)	P(M)	151
18p	LK970	FX1367F	4-5	F	P(M)	P(M)	259
18q	LK1084	T232D	1-2	P(M)	F	F	74
18r	LK1084	FX1367F	1-2	P	F	F	149
18s	TS100	T232D	5	F	F	F	28
18t	TS100	FX1367F	5	F	F	F	35
18u	XP-4-49	T232D	4-5	P(M)	P	P	148
18v	XP-4-49	FX1367F	4-5	P	P	P(M)	199
18w	XP-4-50	T232D	5	P(M)	P	P	118
18x	XP-4-50	FX1367F	5	P	P	P(M)	127

EXAMPLES 19a-19x

Various Anionic Polymers Applied to Nylon 6,6 at 0.5% solids and a pH of 1.8

35

Examples 19a-19x were performed the same as examples 18a-18x with the sole exception that half the amount of anionic polymer was added to the liquor so that it was applied at 0.5% by weight solids. The results of the tests are

shown in Table 19. These results are similar to those for examples 18a-x. Thus, there was not a marked improvement in fluorocchemical performance with the reduced level of anionic binding polymer.

In example 20a, the carpet was the nylon carpet referred to above. After the dyeing step, the carpet was passed through a flex nip applicator to apply both a fluorocchemical and a stainblocker (SST). The bath included 0.142 percent

TABLE 19

Ex. No.	Anionic Polymer	FC Used	AR 40	Oil	Water	Water/ Alcohol	ppm F
19a	FX369	T232D	5	F	F(M)	F	41
19b	FX369	FX1367F	5	F	F(M)	F	55
19c	TX368	T232D	5	F	P	F	41
19d	FX656	FX1367F	5	F	F(M)	F	59
19e	FX661	T232D	5	F	F(M)	F	45
19f	FX661	FX1367F	5	F	F(M)	F	48
19g	FX657	T232D	5	P	P	P	137
19h	FX657	FX1367F	5	F(M)	P(M)	F(M)	127
19i	SR300	T232D	4	P	P	P	142
19j	SR300	FX1367F	5	P(M)	P	P(M)	130
19k	LK1027	T232D	4-5	F(M)	P	P(M)	117
19l	LK1027	FX1367F	5	F(M)	P(M)	P(M)	214
19m	LK1028	T232D	4-5	F(M)	P	P	156
19n	LK1028	FX1367F	4-5	F(M)	P	P(M)	174
19o	LK970	T232D	4-5	F	P	P(M)	160
19p	LK970	FX1367F	3	P	P	F	172
19q	LK1084	T232D	1	F(M)	P	P(M)	97
19r	LK1084	FX1367F	1	P(M)	P	P(M)	173
19s	TS100	T232D	4-5	F	F(M)	F	33
19t	TS100	FX1367F	4-5	F	P(M)	F	41
19u	XP-4-49	T232D	4	F(M)	P	P(M)	87
19v	XP-4-49	FX1367F	4-5	F	P(M)	P(M)	201
19w	XP-4-50	T232D	5	F(M)	P	P	85
19x	XP-4-50	FX1367F	5	P	P	P(M)	188

The following generalizations can be made from a review of the data from examples 12-19. First, it appears that the Leukotan 1028 performed the best as the anionic binding/stain resist polymer on the different nylon fibers, at the different levels, and at the different pH levels. The XP-4-50 appears to have the second best performance, with the FX-657 the XP-4-49 and the Leukotan 970 coming in third, fourth and fifth place respectively.

EXAMPLES 20a-20q

Production Scale Tests

Examples 20a-20q were performed to demonstrate the invention on a production scale. These examples were also performed to compare the simultaneous application of fluorocchemical and stain resist compound (Single Step Treatment or SST), with conventional application of the stain resist compound, if any, followed by the topical application by a spray bar of the fluorocchemical, if any.

In the following examples, the carpet used was all made from either a DuPont Type 1150 nylon 6,6 filament yarn or a 1450 type polypropylene yarn. The nylon yarn was Superba heat set and tufted at 25.0 osy. The polypropylene yarn was also Superba heat set and tufted at 34.3 osy. The carpet included a latex adhesive coat and a polypropylene secondary backing both applied by conventional means. As is typical, the carpet was made in a roll about 12 feet wide.

This nylon carpet was dyed by conventional means. In particular, the carpet was passed through a continuous dye line with a wet pick-up of about 400 percent. The dye bath included an anionic surfactant and acid dyes to impart a putty beige color. The pH of the dye bath was 5.5. The carpet was steamed for 3.7 minutes and then rinsed with a wet pick-up of 500 percent and extracted to a wet pick-up of 40 percent.

solids of XP-4-50 and about 0.064 percent solids of FX1367F. The pH of this bath was 1.8. The wet pick-up was about 350 percent, thereby applying about 0.36 percent fluorocchemical based on the weight of the carpet and about 3.42 percent stain resist compound based on the weight of the carpet. The carpet was steamed for 2.7 minutes and then rinsed with a wet pick-up of 500 percent and extracted to a wet pick-up of 40 percent.

The carpet was then dried in an oven set at 240° F. for 1.0 minutes.

Example 20b was the same as example 20a with the exception that only half as much FX1367F was present in the bath, namely a level of 0.032 percent solids.

Example 20c was the same as example 20a with the exception that NRD372 was used as the fluorocchemical at 0.029 percent solids in the place of the FX1367F.

Example 20d was the same as example 20c with the exception that only half as much NRD372 was used, namely 0.014 percent solids.

Example 20e was the same as example 20a with the exception that T232D was used as the fluorocchemical at a level of 0.010 percent solids.

Example 20f was the same as example 20e with the exception that the level of T232D in the treatment bath was increased to 0.021 percent solids.

Example 20g was the same as example 20e with the exception that the level of T232D in the treatment bath was increased to 0.043 percent solids.

Example 20h was the same as example 20a with the exception that there was no fluorocchemical in the treatment bath. Instead, the treatment bath included only an anionic polymer/stain resistant composition, namely SR300 at 0.24 percent solids. The treatment bath had a pH of 2.2. After the rinse and extraction step described in example 20a, the FX1367F fluorocchemical was applied by a spray bar (Spray)

which applied a wet pick-up of about 15 percent of an emulsion that contained 1.38 percent solids, resulting in an application of about 0.21 percent fluorochemical based on the weight of the carpet.

Example 20i was the same as example 20h with the exception that the FX1367F was present at 1.22 percent of the emulsion sprayed onto the carpet, thus providing 0.18 percent solids based on the weight of the carpet.

Example 20j was the same as example 20i with the exception that the DuPont fluorochemical NRD372 was applied by the spray bar in place of the FX 1367F. The level of NRD372 was 1.17 percent solids of the emulsion, resulting in an application of about 0.18 percent based on the weight of the carpet.

Example 20k was the same as example 20j with the exception that the level of NRD372 was lowered to 0.72 percent solids, resulting in an application of about 0.11 percent based on the weight of the carpet.

Example 20l was the same as example 20a with the exception that the polypropylene carpet was used in place of the nylon carpet. Also, the polypropylene carpet was not dyed, but rather treated with a solution containing only 0.105 percent anionic surfactant at a pH of 7.5. The carpet was steamed for 3.7 minutes before being rinsed and extracted as described above. In addition, the fluorochemical T232D was used in the treatment bath at a level of 0.015 percent solids. The level of XP-4-50 in the treatment bath was lowered to 0.137 percent solids.

Example 20m was the same as example 20l with the exception that the level of T232D in the treatment bath was increased to 0.030 percent solids.

Example 20n was the same as example 20m with the exception that no anionic polymer/stain resist compound was included in the treatment bath or applied to the carpet in any step.

Example 20o was the same as example 20n with the exception that instead of applying T232D fluorochemical in the treatment bath, FX1367F was applied through a spray bar. In particular, the carpet was subjected to the pre-treatment, but not immersed in a bath with either anionic binding polymer or fluorochemical, nor was the carpet subjected to the steaming step that would have taken place after that bath. An emulsion containing 1.06 percent solids FX1367F was sprayed on with a wet pick-up of 15 percent, thereby producing about 0.16 percent solids FX1367F based on the weight of the carpet.

The carpet produced in each of the examples was tested for fluorine content, oil, water, and water/alcohol repellency, the Acid Red #40 stain test, the WAQE stain resistance durability test, the Mustard stain test and the Coffee stain test. The results of these tests are reported in part A of Table 20. The carpet produced was also tested in the for Kappa soiling with the AL* being reported. The carpet was also tested for fluorochemical penetration, lightfastness when exposed to Ozone, NOx and Xenon light. The results of these tests are reported in part B of Table 20.

TABLE 20

Ex. No.	SST or Spray	part A						Must. Stain	Coffee Stain Pen.
		ppm F	Oil	Water	Water/ Alc	AR 40	WAQE Stain		
20a	SST	139	P	F(M)	F	5	3	2-3	4
20b	SST	120	P	F	F	5	3	3	4
20c	SST	185	P	P	F(M)	4-5	3	2-3	4
20d	SST	133	P	P	F(M)	4-5	2-3	3	4-5
20e	SST	149	F(M)	P(M)	F(M)	5	3-4	2-3	4-5
20f	SST	312	P	P	P	5	3-4	3	4-5
20g	SST	971	P	P	P	5	3-4	3	4
20h	Spray	185	P	P(M)	F(M)	4	2-3	1-2	4
20i	Spray	152	P	P(M)	F(M)	4	2-3	1-2	4
20j	Spray	778	P	P	P	4	2-3	1-2	4
20k	Spray	46	P	P	P	4	3	1-2	4
20l	SST	197	P	P	P				
20m	SST	412	P	P	P				
20n	SST	242	P	P	P				
20o	Spray	292	P	P	P				

part B

Ex. No.	SST or Spray	KS AL*	FC Pen.	Ozone	Ozone	NOx	40 hrs Xenon
				2 cyc.	5 cyc.		
20a	SST	-14.16	50%	5	5	3-4	4
20b	SST	-14.63	30%	5	4	3-4	4-5
20c	SST	-12.69	100%	5	5	3-4	3-4
20d	SST	-13.15	60%	5	5	3	4
20e	SST	-17.28	15%				
20f	SST	-16.60	80%				
20g	SST	-17.84	100%				
20h	Spray	-12.70	30%	5	5	4	3-4
20i	Spray	-12.15	30%				
20j	Spray	-11.20	50%	4-5	4-5	4	5
20k	Spray	-12.22	20%	5	5	4	4-5

TABLE 20-continued

20i	SST	-10.67	25%
20m	SST	-10.56	95%
20n	SST	-11.69	10%
20o	Spray	-11.67	30%

It is thus seen that a novel, advantageous method of enhancing the repellency of carpet has been discovered. Preferably, the method also includes the simultaneous application of a compound to enhance the stain resistance of the carpet as well. As such, the invention provides a tremendous advantage in that the two treatments can be added simultaneously.

1. claim:

1. A method of treating carpet yarn to enhance its repellency comprising the steps of:

providing carpet yarn comprising polymeric fibers;

providing effective repellency enhancing amounts of an anionic or nonionic fluorochemical compound and an anionic polymer binding compound in an aqueous medium, the aqueous medium having a pH below about 2.0;

immersing the carpet yarn in the aqueous medium; and removing excess water from the carpet.

2. The method of claim 1 wherein the binding compound increases the stain resistance of the carpet fibers.

3. The method of claim 1 wherein the pH is above about 1.0.

4. The method of claim 1 wherein the pH is between about 1.5 and about 1.8.

5. The method of claim 1 wherein the fluorochemical compound is selected from the group consisting of telomeric fluorochemicals and electrochemically fluorinated fluorochemicals.

6. The method of claim 1 wherein the fluorochemical compound is present in an amount between about 0.0035 and about 0.175 percent of the aqueous medium.

7. The method of claim 1 wherein the binding compound is present in an amount between about 0.05 and about 2.5 percent of the aqueous medium.

8. The method of claim 1 wherein the binding compound is a polymer or copolymer of methacrylic acid.

9. The method of claim 8 wherein the polymer or copolymer of methacrylic acid has a number average molecular weight between about 500 and about 20,000.

10. The method of claim 1 further comprising the step of applying heat to the carpet yarn after being removed from the aqueous medium to thereby fix the fluorochemical compound and the binding compound to the polymeric fibers.

11. The method of claim 10 wherein the carpet yarn is heated at a temperature between about 160° and about 260° F. for between about 15 seconds and about 60 minutes.

12. The method of claim 10 wherein the carpet yarn is heated at a temperature between about 180° and about 220° F. for between about 30 seconds and 8 minutes.

13. The method of claim 10 wherein the carpet yarn is heated with steam.

14. The method of claim 10 wherein the ratio of aqueous medium to carpet yarn during the heating step is at least 0.5:1.

15. The method of claim 10 wherein the ratio of aqueous medium to carpet yarn during the heating step is between about 2.1 and about 60:1.

16. The method of claim 1 wherein the carpet yarn tufted into a carpet which carpet is placed in a vessel containing the aqueous medium.

17. The method of claim 16 wherein the carpet is removed from the vessel before the heating step and the ratio of aqueous medium to carpet during the heating step is at least about 0.5:1.

18. The method of claim 17 wherein the ratio of aqueous medium to carpet during the heating step is between about 2:1 to about 10:1.

19. The method of claim 16 wherein the carpet and the aqueous medium are heated in the vessel.

20. The method of claim 19 wherein the ratio of aqueous medium to carpet during the heating step is between about 12:1 to about 60:1.

21. The method of claim 1 wherein the carpet yarn is tufted into a carpet which is pulled through a pool of the aqueous medium under conditions to produce a ratio of aqueous medium to carpet during the heating step of at least 0.5:1.

22. The method of claim 21 wherein the ratio of aqueous medium to carpet during the heating step is between about 2:1 to about 10:1.

23. The method of claim 22 wherein the carpet is immersed in the aqueous medium by use of a flex nip applicator.

24. The method of claim 1 wherein the carpet yarn is tufted into a carpet which is immersed in the aqueous medium by cascading the aqueous medium over the carpet so as to result in a ratio of aqueous medium to carpet of at least about 0.5:1 during the heating step.

25. The method of claim 1 wherein the fibers are made of a polyamide.

26. The method of claim 1 wherein the fibers are made of nylon and include acid dye sites, and wherein the binding compound blocks the acid dye sites to thereby make the nylon fibers stain resistant.

27. The method of claim 1 wherein the face fibers are made of polypropylene.

28. A method of treating carpet to enhance its repellency and stain resistance comprising the steps of:

providing a carpet comprising nylon face fibers;
providing effective repellency enhancing amounts of an anionic or nonionic fluorochemical compound and an anionic polymer stain resin compound in an aqueous medium, the aqueous medium having a pH below about 2.0;

immersing the carpet in the aqueous medium;
heating the carpet and aqueous medium; and
removing excess water from the carpet.

29. The method of claim 28 wherein the pH is between about 1.5 and about 1.8.

30. The method of claim 28 wherein the fluorochemical compound is selected from the group consisting of telomeric fluorochemicals and electrochemically fluorinated fluorochemicals.

31. The method of claim 28 wherein the fluorochemical compound is a telomeric fluorochemical.

32. The method of claim 28 wherein the fluorochemical compound is present in an amount between about 0.0035 and about 0.175 percent of the aqueous medium.

33. The method of claim 28 wherein the carpet is heated at a temperature between about 180° and about 220° F. for between about 15 seconds and about 6 minutes.

34. The method of claim 28 wherein the carpet is heated with steam.

35. The method of claim 28 wherein the ratio of aqueous medium to carpet yarn during the heating step is at least 0.5:1.

36. The method of claim 28 wherein the ratio of aqueous medium to carpet during the heating step is between about 2:1 and about 60:1.

37. The method of claim 28 wherein the carpet is immersed in the aqueous medium by placing the carpet in a vessel containing the aqueous medium.

38. The method of claim 37 wherein the ratio of aqueous medium to carpet during the heating step is between about 2:1 to about 10:1.

39. The method of claim 38 wherein the carpet and the aqueous medium are heated in the vessel.

40. The method of claim 28 wherein the carpet is immersed in the aqueous medium by pulling a long roll of the carpet through a pool of the aqueous medium under conditions to produce a ratio of aqueous medium to carpet during the heating step of at least 0.5:1.

41. The method of claim 40 wherein the ratio of aqueous medium to carpet during the heating step is between about 2:1 to about 10:1.

42. The method of claim 40 wherein the carpet is immersed in the aqueous medium by use of a flex nip applicator.

43. The method of claim 28 wherein the polyamide is nylon 6.

44. A method of treating polypropylene carpet to enhance its repellency comprising the steps of:

providing a carpet comprising polypropylene face fibers; providing effective repellency enhancing amounts of an anionic or nonionic fluorochemical compound and an anionic polymer binding compound in an aqueous medium, the aqueous medium having a pH below about 3.5;

immersing the carpet in the aqueous medium; heating the carpet and aqueous medium; and removing excess water from the carpet.

45. The method of claim 44 wherein the pH is above about 1.0 and below about 3.5.

46. The method of claim 45 wherein the pH is between about 1.5 and about 1.8.

47. The method of claim 44 wherein the fluorochemical compound is selected from the group consisting of telomeric fluorochemicals and electrochemically fluorinated fluorochemicals.

48. The method of claim 44 wherein the fluorochemical compound is a telomeric fluorochemical.

49. The method of claim 44 wherein the fluorochemical compound is present in an amount between about 0.0035 and about 0.175 percent of the aqueous medium.

50. The method of claim 44 wherein the carpet is heated at a temperature between about 180° and about 220° F. for between about 15 seconds and about 6 minutes.

51. The method of claim 44 wherein the carpet is heated with steam.

52. The method of claim 44 wherein the ratio of aqueous medium to carpet yarn during the heating step is at least 0.5:1.

53. The method of claim 44 wherein the ratio of aqueous medium to carpet during the heating step is between about 2:1 and about 60:1.

54. The method of claim 44 wherein the carpet is immersed in the aqueous medium by placing the carpet in a vessel containing the aqueous medium.

55. The method of claim 54 wherein the carpet is removed from the vessel before the heating step and the ratio of aqueous medium to carpet is at least about 0.5:1.

56. The method of claim 55 wherein the ratio of aqueous medium to carpet during the heating step is between about 2:1 to about 10:1.

57. The method of claim 54 wherein the carpet and the aqueous medium are heated in the vessel.

58. The method of claim 44 wherein the carpet is immersed in the aqueous medium by pulling a long roll of the carpet through a pool of the aqueous medium under conditions to produce a ratio of aqueous medium to carpet during the heating step of at least 0.5:1.

59. The method of claim 58 wherein the ratio of aqueous medium to carpet during the heating step is between about 2:1 to about 10:1.

60. The method of claim 58 wherein the carpet is immersed in the aqueous medium by use of a flex nip applicator.

61. The method of claim 44 wherein the carpet is immersed in the aqueous medium by cascading the aqueous medium over the carpet so as to result in a ratio of aqueous medium to carpet of at least about 0.5:1 during the heating step.

62. A composition for treating carpet to enhance its repellency comprising effective repellency enhancing amounts of:

an aqueous medium;
an anionic or nonionic fluorochemical;
an anionic polymer binding compound;

wherein said aqueous medium has a pH below about 2.0.

63. The composition of claim 62 wherein the fluorochemical compound is present in an amount between about 0.0035 and about 0.175 percent.

64. The composition of claim 62 wherein the anionic polymer binding compound is present in an amount between about 0.01 and about 2.5 percent.

65. The composition of claim 62 having a pH of between about 1.5 and about 1.8.

66. The composition of claim 62 wherein the anionic polymer binding compound is a polymer or copolymer of methacrylic acid.

67. The composition of claim 62 wherein the fluorochemical is selected from the group consisting of telomeric fluorochemicals and electrochemically fluorinated fluorochemicals.

* * * *



US005403362A

United States Patent [19]

Gurley

[11] Patent Number: 5,403,362

[45] Date of Patent: Apr. 4, 1995

[54] MORDANT AND METHOD OF DYEING FIBERS

[75] Inventor: Sally Gurley, Boulder, Colo.

[73] Assignee: Allegro Natural Dyes Inc., Longmont, Colo.

[21] Appl. No.: 59,544

[22] Filed: May 10, 1993

[51] Int. Cl. 6 D06P 1/34; D06P 1/36; C09B 65/00

[52] U.S. Cl. 8/646; 8/653; 8/918; 8/921

[58] Field of Search 8/618, 625, 653, 646, 8/425, 452, 453, 625, 653, 646, 918, 921

[56] References Cited

U.S. PATENT DOCUMENTS

192,201	6/1877	Van Skelline .
671,760	4/1901	Florin .
1,273,293	7/1918	Warkup .
1,565,515	12/1925	Seyer .
1,757,066	5/1930	Watson .
2,152,182	3/1939	Ellis .
2,991,143	7/1961	Rosenblind .
4,283,198	8/1981	Fletcher .
4,486,237	12/1984	Paffoni et al. .
4,756,037	7/1988	McFadyen et al. .
4,845,789	7/1989	Morton et al. .
4,882,140	11/1989	Becker .

OTHER PUBLICATIONS

Crews, P., Part I. Considerations in the Selection and Application of Natural Dyes: Mordant Selection; Shuttle, Spindle & Dyepot 12:15,62 (Spring, 1981).

J. Greene, "Plant Dyes for Homespun Color," Horticulture Aug. 1978.

R. Smith and S. Wagner, "Dyes and the Environment: Is Natural Better?" Amer. Dyestuff Rep. 80(9):32 (Sep. 1991).

P. M. Suave, "Natural Dyes in Quebec," Color Res. & Appl. 6:172-173 (Fall 1981).

R. N. Padhye and D. Rathai, "Effect on Mordant Dyeing of Cotton with Vegetable Dyes," Textile Dyer & Printer 23(25):27-28 (Dec. 12, 1990).

A. Sayeed, et al., "Jute Fiber Dyeing with Catechu

Tannic Acid and Catechin," Indian Textile J. 100(9):114-119 (Jun., 1990).

D. Bahl, et al., "Development of Dyeing Process of Silk with Natural Dye-Cutch," Colourage 35(22):22-24 (Nov. 16, 1988).

V. A. A. Shenai, et al., "Studies on Natural Dyes, Part II, Dyeing and Printing of Cotton Cloth with Ain Bark Extract by Suitable After-Treatments," Textile Dyer & Printer 12:29-31 (Jun., 1979).

A. Garg, et al., "Effect of Mordants on Color of Natural Dye Extracted from Tissue Flowers (*Butea monosperma*)," Colourage 38(3):50-53 (Mar., 1991).

S. J. Rama and K. C. Gupta, "Parijataka-a good source of dye for woollens," Textile Dyer & Printer 23(25):27-28 (Dec. 12, 1990).

S. Vednere, et al., "Teak leaves and chir bark as natural

(List continued on next page.)

Primary Examiner—Paul Lieberman
Assistant Examiner—Margaret Einsmann
Attorney, Agent, or Firm—Howard & Howard

[57] ABSTRACT

An improved mordant solution and process for preparing fibers for dyeing and fixing natural dyes to fibers, particularly but not exclusively cellulose fibers, including cotton and linen, and synthetic fibers, including Rayon ® and Tencel™. The improved natural mordant solution comprises an aqueous solution of alum $KAl(SO_4)_2$ and soda ash Na_2CO_3 , most preferably an aqueous colloidal suspension of aluminum hydroxide. This mordant solution significantly improves the recognized measurable qualities of naturally dyed fibers, including light and washfastness, without using polluting heavy metal mordants. The improved mordant treatment and natural dye process includes first pretreating the fabric with an aqueous mordant wash, which increases the dye uptake in the dye bath, then treating the fabric with a second aqueous mordant wash, following dyeing, then preferably treating the dyed fabric with a final tannin wash, permanently setting the natural dye in the fibers or fabric.

10 Claims, No Drawings

OTHER PUBLICATIONS

dyes for wool," *Colourage* 37(20):48-49 (Dec., 1990).
Simmons, Max, "The Mordant Process," *Dyes and Dyeing*, (no month available 1978) Van Nostrand Reinhold, Australia.
Liles, J., *The Art and Craft of Natural Dyeing*, pp. 3-5, Appendix B, University of Tennessee Press (no month

available 1990).
Bliss, Anne, *A Handbook of Dyes from Natural Materials*, Chapter 2, pp. 21-25, 37-39; Charles Scribner's Sons (no month available 1981).
Brunello, Franco, *The Art of Dyeing in the History of Mankind*, p. 308, Neri Pozza Editore (no month available 1973).

MORDANT AND METHOD OF DYEING FIBERS

BACKGROUND OF THE INVENTION

This invention relates to an improved mordant solution which is particularly suitable for dyeing cellulose fibers, such as cotton and linen, without the use of dangerous and polluting heavy metal salt or iron mordants. The method of this invention further includes a process for dyeing such fibers using natural dyes and nonpolluting mordants.

The use of synthetic dyes began with Perkin's accidental synthesis of mauvein (C_7H_2Na) or "aniline purple" in 1856. Perkin was attempting to synthesize quinine, but recognized the commercial potential of mauvein as a synthetic dye. The synthetic dye industry was the major synthetic organic chemical industry in the early 1900's. Synthetic dyes have now largely replaced natural or vegetable dyes in the textile industry, relegating natural dyes to use by hobbyists and cottage industries. The annual global sales of synthetic dyes are now estimated to be about \$20,000,000,000.

Production and use of synthetic dyes however produces serious toxic waste problems. The dye industry has recently attempted to reduce toxic effluents by recharging dyebaths, using different dye techniques that are more efficient, recycling and recovering waste, and using computer technology to control the introduction of dyes and chemicals in the bath. Exhaustion rates have been improved in certain facilities to above about 65%; however, the average exhaustion rate remains about 40% and the synthetic dye industry continues to be a major source of pollution, discharging heavy metal salts and other toxic waste into the environment.

Because of the problems associated with synthetic dyes, there has been a renewed interest in natural or vegetable dyes. Natural dyes, such as indigo, tannin and madder have been used since the beginning of recorded history; however, it is almost impossible using known techniques to obtain the same dye shade twice in succession with natural dyes, even using the same method. As noted by a major synthetic dye manufacturer, the color-giving molecules in the plants used for dyeing have not been "specifically designed by nature" for transfer to a substrate. Using prior natural dyeing processes, it is often necessary to choose conditions which severely damage the fiber to obtain a suitably dyed fabric. Further, it has not been possible to obtain dyed fabrics which are light and washfast and it has not been possible to obtain a full palette of colors, using natural dyes. Thus, the textile industry has generally rejected natural dyes for commercial applications.

The most commonly used mordants for natural dyes are also potential sources of toxic waste. Mordants are chemicals that are necessary to chemically fix most natural dyestuffs. The mordant combines with both the dye molecule and the fiber molecule, producing a permanently fixed insoluble "color lake." The insoluble mordant-dye complex that is chemically combined with the fiber in a mordant dyed fiber is referred to as a color lake. Color lakes are produced with adjectice dyes. Color lakes produced by reacting a dye with a metallic salt, such as madder (alizarin) with alum, were also used in inks and paints. The most commonly used mordants for natural dyes are alum or potassium aluminum sulfate, chrome or potassium dichromate or potassium bichromate, blue vitriol or copper sulfate, ferrous sulfate, stannous chloride, sodium dithionite or sodium

hydro sulfite, ammonium hydroxide, cream of tartar or potassium bitartrate, "Glauber's salt" or sodium sulfate, lime, lye or sodium hydroxide, oxalic acid, tannic acid, uria, vinegar or acetic acid and washing soda or sodium carbonate. As will be understood, several of these mordants produce toxic waste, but the prior art has failed to produce permanently dyed cellulose fibers or fabric which are color and washfast and which produce a wide range or palette of colors, even using heavy metal salt mordants.

Thus, there is an urgent need for a natural dye process which can meet the needs of the commercial textile industry, including a full palette of consistently reproducible natural colors, which are wash and lightfast. Further, there is an urgent need for a mordant and dye process which does not produce toxic wastes. The mordant and dye process of this invention meets both of these urgent needs.

SUMMARY OF THE INVENTION

The improved mordant of this invention may be used for pretreatment of fibers, including cellulose fibers, for dyeing and for setting of natural dyes in such fibers, including, for example, cotton and linen fabrics and synthetic textiles which are often difficult to dye, including Rayon ® and Tencel™ fibers and textiles. The improved nonpolluting mordant of this invention comprises all aqueous solution of alum or potassium aluminum sulfate ($KAl(SO_4)_2 \cdot 12H_2O$) and soda ash (Na_2CO_3). The most preferred mordant solution of this invention comprises a colloidal suspension of aluminum hydroxide in aqueous solution, wherein the concentration of alum is about seven times the concentration of soda ash, in weight percent. The preferred mordant colloidal suspension may be formed by adding alum to an aqueous solution of soda ash in water, agitating and heating the solution to about 150° F. In a typical application using a dye liquor containing the vegetable dye Osage, the second mordant solution may contain 0.45% by weight soda ash and 3% by weight alum. In another example where the dye liquor includes the vegetable dyes Madder or Cutch, the second mordant solution contains 0.3% by weight soda ash and 2% by weight alum.

The preferred method or process of this invention for permanently dyeing fibers, including natural cellulose fibers, includes pretreating the fibers with a mordant solution comprising an aqueous solution of alum and soda ash. The pretreated or premordanted fibers are then treated, following washing, with a dye liquor preferably containing a natural dye. The fibers are then treated with a second mordant solution, which is also preferably an aqueous solution of alum and soda ash, as described. The second mordant solution is preferably added directly to the dye bath, near the end of the dye treatment cycle. Finally, the fibers are preferably treated with a weak solution of tannic acid, further setting the natural dye in the fibers.

More specifically, the disclosed natural dye process includes first pretreating the fibers by wetting the fibers with a commercially available wetting agent, then immersing and agitating the fibers in the presence of the aqueous mordant solution, preferably at a temperature of about 110° to 170° F. for about an hour. In the most preferred method of pretreatment, the fibers are treated with the mordant in temperature stages, first at a lower temperature of for example 120° F. for about twenty

minutes, then at a higher temperature for example 140° F. for about ten minutes and finally at about 165° F. for about 45 minutes. This results in improved dye uptake and clearer effluent. The liquid is then drained and the fibers are rinsed with warm water and preferably dried. The pretreated or premordanted fibers are then treated with a dye, preferably an aqueous natural dye liquor, for sufficient time to produce the desired color. The fibers are then treated with a second mordant solution, preferably an aqueous solution of alum and soda ash, as described. The second mordant solution may be added directly to the dye liquor, preferably near the end of the dye treatment cycle; for example, in the last fifteen minutes. The dye liquor is then drained. In the most preferred method of dyeing natural cellulose fibers, the fibers are finally treated with a weak aqueous solution of tannin or tannic acid containing about 1% tannic at a temperature of about 140° F., which further sets the natural dye in the fibers. The fibers are then rinsed, drained and dried.

The improved mordant solution and natural dye process of this invention produces permanently dyed fibers and fabrics or textiles which are light and washfast and can be used to produce a full palette of reproducible natural colors. Further, the mordant and dye process of this invention does not require the use of heavy metal salts or iron and thus produces permanently dyed fibers in a wide range of colors without producing toxic waste. Finally, the mordant natural dye process of this invention requires significantly less energy than commercial dye processes. The mordant solution and natural dye process of this invention thus solves the problems with the prior natural dye processes and avoids the pollution and toxic waste problems associated with synthetic dyes. Other advantages and meritorious features of this invention will be more fully described in the following description of the preferred embodiments of the mordant solution and natural dye process of this invention which follows and the appended claims.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF IMPROVED MORDANT AND NATURAL DYE MORDANT PROCESS OF THIS INVENTION

As described, the improved nonpolluting mordant solution of this invention is particularly, but not exclusively suitable for dyeing natural cellulose fibers, including cotton and linen. Natural dye mordant processes were used long before the introduction of synthetic dyes in the late mid 19th century. The mordant and natural dye mordant process of this invention may be used with many natural or vegetable dyes, some of which had been used since before recorded history. Natural dyes which may be used in the dye process of this invention include, but are not limited to madder, 45 cochineal, cutch and osage. Madder is a vegetable dye produced from species of Rubis, herbaceous perennials grown in Europe and Asia. Preparations of dyes from madder root were used to produce red, yellow and brown colorations prior to the introduction of synthetic dyes. The mordants used with madder dyes included chromium, aluminum, iron, copper, tin and other heavy metal and polluting salts. Cochineal is an insect dyestuff indigenous to Mexico, which was in use by natives when the Spaniards invaded Mexico in 1518. The insect 50 cochineal is the *Coccus cacti* which is cultivated in Mexico, Peru and other countries for producing carmine red. Stannous chloride was the principal mordant used

with cochineal. Cutch or Catechu, also known as *Terra japonica*, is obtained from various species of Mimosa, Acacia and Areca trees chiefly found in India, Southern Asia and Africa. The commercial dye product is an extract obtained by boiling the wood, trees, leaves and fruit and processed to produce a yellow or olive color, depending upon the mordant used. The mordant solution of this invention may also be used with indigo; however, the indigo dye process is described in a separate patent application filed concurrently herewith. The methods of processing and preparing dye liquors from madder, cochineal, cutch, indigo and other natural dye substances are well documented in the literature and such processes are not, therefore, described herein.

As described above, the improved mordant of this invention may be used both for pretreating or premordanting the fibers, prior to dyeing and for mordanting, following dyeing. The preferred mordant solution is an aqueous solution of alum and soda ash. More specifically, the preferred mordant solution of this invention comprises a colloidal suspension of aluminum hydroxide in aqueous solution, wherein the concentration of alum is about seven times the concentration of soda ash, in weight percent. This colloidal suspension may be formed by first adding fiber soda ash to water to form an aqueous solution of soda ash. Fiber alum or potassium aluminum sulfate is then slowly added to the aqueous solution of soda ash while the solution is agitated and heated to about 150° F. The colloidal suspension begins to form at about 140° F.

The fibers to be dyed, which may be in the form of a garment, pieces of textile or yarn, is then pretreated with the mordant solution, as follows. First, the fibers are wetted out by agitating the fibers with a commercial wetting solution, such as "Ecowet" available from Southeast Chemical Corp. The fibers are then agitated in the mordant solution and heated to about 165° F. In the most preferred premordant process, the fibers are immersed in the mordant solution which is first heated to about 120° F. and agitated for about ten minutes. The mordant solution is then heated to about 140° F. and agitated for an additional ten minutes. Finally, the mordant solution is heated to about 165° F. and agitated for about forty-five minutes. The mordant solution is then drained, the fibers are rinsed in warm water and dried. The fibers are now ready for dyeing.

After wetting the fibers, the fibers are immersed and agitated in an aqueous solution of the natural dye liquor for a time sufficient for uptake of the dye. A second mordant solution is then introduced, preferably near the end of the dye cycle and the fibers are agitated in the mordant and dye solutions for about fifteen minutes. Finally, the fibers are preferably agitated in a weak aqueous solution of tannic acid or tannin.

The mordant solution and natural dye mordant process of this invention will be more fully understood from the following examples. 9,100 gms or about twenty pounds of cotton garments were pretreated or premordanted with the nonpolluting mordant solution of this invention, as follows. Two percent of the weight of the fibers or 182 gms of soda ash was added to five gallons of warm water and stirred to dissolve all of the soda ash in solution. Fifteen percent of the weight of the fibers or 1,365 gms of alum was then added slowly to the aqueous solution of soda ash to avoid flashing. The solution was then heated to about 150° F. and stirred to form a colloidal suspension of aluminum hydroxide in water.

The fibers are then pretreated by first wetting out the fibers with warm water and 40 ml of "Ecowet" commercial wetting solution. The fibers are then heated to 120° F., and one-half of the premordant solution was added and the fibers were agitated for ten minutes. The fibers and mordant solution was then heated to 140° F., the remainder of the mordant solution was added and the fibers were agitated in the mordant solution for an additional ten minutes. The aqueous mordant solution was then heated to 165° F. and agitated for an additional forty-five minutes. The fibers and solution were then cooled to 120° F., drained, rinsed and dried.

The natural dye mordant process of this invention may be carried out in a conventional commercial or industrial washing machine. A computer control industrial washing machine may be preferred which allows the operator to preprogram the introduction of fluids, such as water into the washing machine chamber or basket, temperature and time, including wash and agitation cycles, etc. Further, it is possible to program an industrial washer to ramp up or down the temperature while agitating the fibers, as described herein. A suitable industrial washing machine for the natural dye mordant process of this invention is the Unimac Washer Extractor made by Unimac Corporation; however, the process of this invention is not limited to any particular machine or equipment. In fact, the natural dye mordant process of this invention may be adapted to existing dye apparatus and processes, including package dye machines.

Cotton fibers in the form of garments were dyed with cochineal, as follows. Twenty pounds (9,100 gms) of pretreated cotton fibers in the form of garments were first wetted out with warm water containing 40 ml of "Ecowet" commercial wetting solution. One gallon (2.79 liters) of water containing cochineal dye extract was added to the wetted out fibers and heated at two degrees per minute to 165° F. The fibers were then agitated in the aqueous dye solution for thirty-five minutes. A second aqueous mordant solution containing 0.3% soda ash (27.3 gms) and 2% weight of fibers (182 gms) was added and the fibers were agitated for fifteen minutes. The second mordant solution was prepared as described above to produce a colloidal suspension of aluminum hydroxide.

The dye mordant solution was then drained and an aqueous solution containing 1% weight of fiber (91 gms) tannin was added to the chamber. The chamber was then heated to 140° F. and agitated for ten minutes. The tannin solution was then drained, the fibers were washed with detergent, rinsed and dried.

The same procedure was used to dye pretreated fibers with osage, except that 15% weight of fibers osage dye extract or 2.33 gallons was added to the pretreated fibers after wetting and the second mordant solution contained 0.45% weight of fibers (41 gms) soda ash and 3% weight of fibers (273 gms) of alum was prepared as described to produce an aqueous colloidal suspension of aluminum hydroxide.

Although the manufacture and use of synthetic dyes remains a major source of pollution, the commercial textile industry has rejected natural or vegetable dyes because such dyes are not reproducible and the dyed fabrics are not light and washfast using present methods. Protein fibers, such as wool, are somewhat easier to dye and natural dyes are used to a limited extent to dye protein fibers. Further, as set forth above, indigo remains in use for dyeing denim yarn. However, cotton is

the primary natural fiber used by the garment industry, accounting for nearly fifty percent of the fibers used. There is, however, no natural dye mordant process for dyeing cotton fibers, fabric or garments which results in a wash and lightfast garment.

The mordant dye process of this invention does produce consistent dyed yarns, textile pieces and garments in a wide range of natural colors. Further, the colors are wash and lightfast. The American Association of Textile Colorists and Chemists have developed standardized tests to determine whether a dyed fabric is washfast (Test No. 61A) and lightfast (Test No. 16E). The potential score or index on such tests range from 0 to 5. Fabrics dyed with natural dyes using conventional natural dye mordant processes score only 1 or 2 on the light and washfast tests for cotton fabrics; however, synthetic dyes generally score about 4 or even greater on such tests. The natural dye mordant process of this invention, however, results in a dyed fabric which scores between 3 and 5 on such tests, equal to or greater than synthetic dyes on the same fabrics. Further, as set forth above, the natural dye mordant process of this invention does not result in pollution.

As will be understood by those skilled in the art, certain modifications can be made to the nonpolluting mordant and natural dye mordant process of this invention within the purview of the appended claims. The natural dye mordant process of this invention is not limited to the natural dyes disclosed herein, but may be used for other dyes. Further, the natural dye mordant process is not limited to dyeing cotton or other cellulose fibers, although the process of this invention is very successful with cellulose fibers, which are difficult to dye, particularly with natural dyes. The process of this invention may also be used with some synthetic yarns and fabrics. Finally, the improvements in the nonpolluting mordant solution and natural dye mordant process of this invention may be used individually or in combination to produce improved dyed fibers or fabric. For example, the use of a final tannin treatment following the dye-mordant step resulted in a 10 to 20% improvement in wash and lightfastness. The use of an aqueous colloidal suspension of aluminum hydroxide resulted in a 20 to 40% improvement in such tests and the use of a second mordant treatment resulted in a further 10% improvement. As will be understood, these improvements were unexpected, particularly in view of the long history of the use of natural dyes and the replacement of natural dyes by synthetic dyes over a century ago.

I. claim:

1. A process for permanently dyeing fibers, fabrics and textiles selected from the group consisting of cotton, linen and other cellulose fibers, said process comprising the following steps:

pretreating said fibers at a temperature between about 110° F. and about 170° F. with a mordant comprising an aqueous colloidal suspension formed by adding soda ash and alum to warm water wherein the concentration of alum is about seven times the concentration of soda ash in weight percent and wherein the mordant is present in an amount sufficient to fix a natural dye; and
treating said fibers with an aqueous solution containing a natural dye liquor wherein the natural dye is present in an amount sufficient to permanently dye said fibers.

2. The process for permanently dyeing fibers as defined in claim 1, wherein said process further includes treating said fibers with said mordant following dyeing.

3. The process for permanently dyeing fibers as defined in claim 2, wherein said process further includes 5 treating said fibers with an aqueous solution of tannic acid following treating said fibers with said mordant following dyeing.

4. The process for permanently dyeing fibers as defined in claim 1, wherein said mordant is formed by 10 adding alum to an aqueous solution of soda ash, agitating and heating said solution to a temperature of at least about 150° F.

5. The process for permanently dyeing fibers as defined in claim 1, wherein said mordant is formed by first 15 adding soda ash to water, forming an aqueous solution of soda ash in water, then adding alum to said solution, agitating and heating said solution to form said colloidal suspension.

6. A process for permanently dyeing fibers, fabrics 20 and textiles selected from the group consisting of cotton, linen, and other cellulose fibers, comprising the following steps:

pretreating said fibers by immersing said fibers in water containing a mordant which comprises an 25 aqueous colloidal suspension formed by first adding soda ash to said water, then adding alum to form a colloid suspension, wherein the concentra-

tion of alum is about seven times the concentration of soda ash, in weight percent, and wherein the mordant is present in an amount sufficient to fix a natural dye, and agitating said fibers at a temperature of at least about 110° F. to about 170° F.; treating said fibers with an aqueous solution containing a natural dye liquor in an amount sufficient to permanently dye said fibers; and treating said fibers with said mordant solution to further bond said dye to said fibers.

7. The process of permanently dyeing fibers as defined in claim 6, wherein said mordant is formed by adding alum to an aqueous solution of soda ash at a temperature of about 120° to 170° F.

8. The process of permanently dyeing fibers as defined in claim 6, wherein said process further includes treating said fibers with an aqueous solution of tannic acid following said treatment of said fibers with said second mordant solution.

9. The process of permanently dyeing fibers as defined in claim 8, wherein said second mordant solution is added to said fibers near completion of dye treatment.

10. The process of permanently dyeing fibers as defined in claim 6, wherein said mordant is formed by adding alum to an aqueous solution of soda ash and water, agitating and heating said mixture to form said colloidal suspension.

* * * * *

30

35

40

45

50

55

60

65